

THE SPIRIT OF CHEMISTRY

*BY THE SAME AUTHOR*

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# FIGURES IN THE TEXT

FIG.	PAGE
1. Early apparatus for distillation . . . . .	24
2. Filtration . . . . .	39
3. Distillation . . . . .	40
4. Manley's reaction vessel . . . . .	53
5. Allegorical representation of the solution of gold by <i>aqua regia</i> . . . . .	59
6. Periodic classification of the elements . . . . .	72
7. Crookes tube . . . . .	76
8. X-ray tube . . . . .	78
9. Gold-leaf electroscope . . . . .	79
10. Fog-tracks of alpha particles . . . . .	82
11. Diagram of atomic constitution . . . . .	92
12. Hales' apparatus for collecting gases . . . . .	97
13. Diffusion . . . . .	99
14. Boyle's tube . . . . .	99
15. Hero's device for automatically opening a Temple door . . . . .	101
16. Distribution of small particles in a suspension . . . . .	114
17. Wire gauze floating on the surface of water . . . . .	117
18. Vapour pressure of liquids . . . . .	119
19. Increase of vapour pressure with temperature . . . . .	119
20. Critical temperature of ether . . . . .	121
21. Hampson apparatus for liquefying air . . . . .	122
22. Dewar vacuum vessel . . . . .	123
23. Growth of crystals . . . . .	125
24. Snow crystals . . . . .	127
25. X-ray examination of crystals . . . . .	129
26. Arrangement of atoms in the diamond crystal . . . . .	129
27. Arrangement of atoms in the crystal of sodium chloride . . . . .	130
28. Foot-bellows used in ancient times by Egyptians . . . . .	138
29. Mayow's apparatus . . . . .	140
30. Lavoisier's experiment of heating mercury in air . . . . .	144
31. Scheele's apparatus for the preparation of oxygen . . . . .	148
32. Preparation of oxygen . . . . .	152
33. Preparation of carbon dioxide . . . . .	155
34. Preparation of argon . . . . .	162
35. Formation of a spectrum . . . . .	163
36. Spectroscope . . . . .	164
37. Spectrum of helium . . . . .	164
38. Extinction of flame by wire gauze . . . . .	169
39. Miner's safety lamp . . . . .	170
40. Coal gas burning in air, and air in coal gas . . . . .	173
41. Electric furnace for the production of phosphorus (diagrammatic) . . . . .	175
42. Ozone apparatus . . . . .	191

FIG.	PAGE
43. Diagram of gas-manufacturing plant . . . . .	212
44. Bunsen burner . . . . .	216
45. Gas cooker, constructed on the principle of the Bunsen burner . . . . .	216
46. Blowpipe . . . . .	216
47. Kipp's apparatus . . . . .	221
48. Electrolytic decomposition of water . . . . .	222
49. Solubility of salts in water . . . . .	237
50. Osmotic pressure . . . . .	239
51. Pfeffer's osmometer . . . . .	241
52. Osmotic pressure and plant cells . . . . .	242
53. Conductivity of solutions for electricity . . . . .	250
54. Migration of ions . . . . .	265
55. Daniell cell . . . . .	268
56. Leclanché cell . . . . .	270
57. Dry cell . . . . .	271
58. Nelson cell . . . . .	275
59. Carborundum furnace . . . . .	280
60. Leaf-like crystals of zinc . . . . .	286
61. Crystalline structure of metals . . . . .	287
62. Section of blast furnace (diagrammatic) . . . . .	293
63. Steel with needles of cementite . . . . .	299
64. Steel with needles of cementite, after being worked . . . . .	300
65. Damascus steel . . . . .	300
66. Season cracking of brass . . . . .	304
67. Catalytic surface of nickel . . . . .	331
68. Frasch method of winning sulphur . . . . .	337
69. Rhombic crystals of sulphur . . . . .	339
70. Monoclinic crystals of sulphur . . . . .	339
71. Priestley's flask for sulphur dioxide . . . . .	341
72. Preparation of sulphur dioxide . . . . .	342
73. Desiccator . . . . .	347
74. Solubility curves of the chlorides and nitrates of potassium and sodium . . . . .	355
75. Preparation of nitric acid . . . . .	363
76. Preparation of nitrous oxide . . . . .	366
77. Dialyser . . . . .	384
78. Iceland spar, showing double refraction . . . . .	389
79. Ultra-microscope . . . . .	403
80. Preparation of ether . . . . .	431
81. Starch grains under the microscope . . . . .	438
82. Right and left handed spirals . . . . .	443
83. Demonstration of the polarisation of light . . . . .	444
84. Holohedral crystals of paratartronic acid . . . . .	447
85. Crystal showing hemihedral faces . . . . .	447
86. Enantiomorphic crystals of optically active tartrates . . . . .	448
87. Symmetrical tetrahedron and its mirror image . . . . .	450
88. Asymmetric tetrahedron and its mirror image . . . . .	450

# THE SPIRIT OF CHEMISTRY

*An Introduction to Chemistry for Students of  
the Liberal Arts*

BY

ALEXANDER FINDLAY

Professor of Chemistry, University of Aberdeen

*It is not the particular facts of a science that constitute its vitality, but the generic facts or conceptions to which they have elevated the mind. Facts are the body of science, and the idea of those facts is its spirit.*—SAMUEL BROWN

*WITH PORTRAITS AND ILLUSTRATIONS*

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## PREFACE

THIS book has been written as a text-book for those students, more especially, who, in the Universities of Great Britain and in the Colleges of the United States, in increasingly large numbers, pursue a course in chemistry as an element of general culture rather than as a part of their professional or technical training. Its form and content, therefore, have been chosen so as to make appeal to the imagination and intellectual interests of those who are not destined for a scientific career, but who desire to understand something of the intellectual progress of recent years and to gain some knowledge of a branch of science on which much of our present-day civilisation is based.

While it is sought to give, in a historical setting, some account of the more important discoveries and achievements in chemical science, and of the materials and chemical phenomena met with in everyday life, the purpose of the book is not so much to impart a detailed knowledge of a wide range of facts as to create a scientific spirit; a spirit of toleration and of co-operation, of intellectual adventure and of intellectual honesty, which seeks ever to enlarge our knowledge of the external world and to found that knowledge, not on tradition or authority, but on a basis of ascertained fact. It is, moreover, the aim and purpose of this book to give some understanding of the fundamental principles and concepts, and to trace the historical development of law and theory, in chemical science. By means of portraits and of thumbnail biographical sketches, also, it is sought to make the leaders in the development of chemical science live in the mind of the student, not as mere names but as human beings.

The first rough sketch of this work was made some fifteen years ago, in a short course of lectures delivered before an audience of theological students and of the general public, and published under the title *Chemistry in the Service of Man*. The reception given to that book, and the experience gained by lecturing to students of various faculties, encourage me in the

## CHAPTER V

## ATOMIC WEIGHTS AND THE PERIODIC LAW

Döbereiner's triads. Dmitri Ivanowitsch Mendeléeff. Periodic law.  
 Classification of the elements . . . . . p. 68

## CHAPTER VI

## RADIOACTIVITY AND ATOMIC CONSTITUTION

Prout's law. Cathode rays. Radioactivity. Disintegration theory of  
 radioactivity. Atomic structure. The atomic number. Isotopes. Electronic  
 constitution and valency. Transmutation and sub-atomic energy . p. 75

## CHAPTER VII

## THE THREE STATES OF MATTER

The gaseous state. Diffusion. Boyle's law. Gay-Lussac's law. Normal  
 temperature and pressure. Kinetic theory of gases. Molecular theory.  
 Gay-Lussac's law of combination of gases by volume. Amedeo Avogadro.  
 Hypothesis of Avogadro. Gas density and molecular weight. General gas  
 equation. The objective reality of molecules. Brownian movement. Mole-  
 cular magnitudes and Avogadro's number . . . . . p. 96

## CHAPTER VIII

THE THREE STATES OF MATTER (*continued*)

The liquid state. Surface tension. Vapour pressure. Latent heat of  
 vaporisation. Liquefaction of gases. Critical temperature. The crystalline  
 state. Melting-point and freezing-point. Supercooled liquid. Velocity of  
 crystallisation. Dendrites. Crystalline structure . . . . . p. 116

## CHAPTER IX

## THE DETERMINATION OF ATOMIC WEIGHTS

Equivalents. Stanislaw Cannizzaro. Molecular weights as a basis for  
 atomic weights. Atomic heat. Calculation of formulæ . . . . . p. 131

## CHAPTER X

THE GASES OF THE ATMOSPHERE AND THE PHENOMENON OF  
COMBUSTION

Historical. John Mayow. The phlogiston theory. Lavoisier and the overthrow of the phlogiston theory. The gases of the atmosphere. Nitrogen. Carl Wilhelm Scheele. Joseph Priestley. Oxygen. Carbon dioxide. Water vapour. Rare gases. Henry Cavendish. Discovery of argon. William Ramsay. Spectroscopic identification of the rare gases. Helium. Neon, krypton, xenon and radon . . . . . p. 138

## CHAPTER XI

## THE PRODUCTION OF FIRE

Ignition point. Slow combustion. Spontaneous combustion. Production of fire. Phosphorus. Allotropic modifications . . . . . p. 168

## CHAPTER XII

## MATTER AND ENERGY

Forms of energy. Conservation of energy. Heat of reaction. Exothermal and endothermal reactions. Heat of combustion. Carbon monoxide. Reduction. Allotropic forms of carbon. Diamond. Graphite. Charcoal and lampblack. Ozone . . . . . p. 179

## CHAPTER XIII

## FUELS AND ILLUMINANTS

Solid fuels and illuminants. Wood. Calorific value. Coal. Distillation of coal. Coke. Semi-coke. Candles. Liquid fuels and illuminants. Petroleum. Composition of petroleum. Methane. Olefines. Ethylene. Naphthenes. Fractional distillation of petroleum. Kerosene as an illuminant. Oil fuel. Gasoline as a fuel. Production of liquid fuel from shale and coal. Gaseous fuels and illuminants. Natural gas. Coal gas. Luminosity of flame. Water gas. Carburetted water gas. Therm. Bunsen burner. Oxy-coal gas blowpipe. Lime light. Incandescent mantle. Acetylene . . . . . p. 193

## CHAPTER XIV

## HYDROGEN, WATER AND HYDROGEN PEROXIDE

Hydrogen. Preparation of hydrogen. Properties of hydrogen. Water. Natural waters. Potable water. Hard water. Softening of water. Permutit process. Physical properties of water. Composition of water. Some chemical properties of water. Hydrogen peroxide. . . . . p. 220

## CHAPTER XV

## SOLUTIONS

What is a solution? Solubility of gases. Henry's law. Metastable equilibrium. Solubility of liquids. Critical solution temperature. Solubility of solids. Purification by recrystallisation. Diffusion and osmotic pressure. Measurement of osmotic pressure. Jacobus Henricus van't Hoff. Analogy between solutions and gases. Freezing-point of solutions. Boiling-point of solutions . . . . . p. 233

## CHAPTER XVI

## ACIDS, ALKALIS AND SALTS. THEORY OF IONISATION

Abnormal behaviour of solutions. Electrolytes and non-electrolytes. Svante August Arrhenius. Theory of electrolytic dissociation. Definition of acids, alkalis and salts. Degree of ionisation . . . . . p. 248

## CHAPTER XVII

## ELECTRICITY AND CHEMISTRY

Birth and early development of electrochemistry. Humphry Davy. Michael Faraday. Mechanism of electrolysis. Laws of electrolysis. Voltaic cells. Electrical energy. Electromotive force. Electrochemical industries. Electro-plating. Electrolytic preparation of sodium hydroxide and chlorine. Bleaching powder. Sodium hypochlorite. Potassium chlorate. Hydrogen chloride and hydrochloric acid. The halogens. Electrolytic production of hydrogen and oxygen. Electrothermal reactions. Carborundum. Alundum . . . . . p. 257

## CHAPTER XVIII

## METALS AND THEIR PROPERTIES

Metals in antiquity. What is a metal? Metallurgy. The structure of metals . . . . . p. 281

## CHAPTER XIX

## METALS AND ALLOYS

Gold, silver and platinum. Gold. Gold chloride. Silver. Silver nitrate. Silver halides. Platinum. Platinito. Iron and steel. Extraction of iron from its ores. Cast iron, wrought iron and steel. Ferrous and ferric salts. Non-ferrous metals and alloys. Copper. Copper alloys. Salts of



copper. Nickel. Cobalt. Mercury. Tin. Zinc. Lead. Oxides of lead. White lead. Tungsten. Non-ferrous metals produced by electrolysis. The alkali metals. Sodium and potassium. Aluminium. Artificial rubies and sapphires. Magnesium . . . . . p. 288

## CHAPTER XX

### VELOCITY OF REACTIONS AND CATALYSIS

Chemical affinity. Law of mass action. Reversible reactions and equilibrium. Theorem of Le Chatelier. Catalysis. Small causes and great effects. Autocatalysis. Negative catalysis. Catalysis in heterogeneous systems. Enzymes as catalysts. The "poisoning" of catalysts. Mechanism of catalysis. Catalysis in industry . . . . . p. 317

## CHAPTER XXI

### SULPHUR AND SULPHURIC ACID

Sulphur. Production of sulphur. Allotropy of sulphur. Sulphur dioxide and sulphurous acid. Sulphuric acid. The lead chamber process. The contact process. Properties of sulphuric acid . . . . . p. 334

## CHAPTER XXII

### SALTS OF POTASSIUM AND SODIUM

Salts of potassium. Potassium nitrate and sodium nitrate. Sodium carbonate. Sodium chloride . . . . . p. 350

## CHAPTER XXIII

### NITROGEN. THE PRODUCTION OF FERTILISERS AND EXPLOSIVES

Nitric acid. Oxides of nitrogen. Nitrous oxide (laughing gas). Ammonia. Use in refrigeration. Nitric acid from ammonia. Nitrogenous fertilisers. Explosives. Gun-cotton. Fulminate of mercury. Nitroglycerine. Dynamite. Blasting gelatine. Cordite. Picric acid. Trinitrotoluene. Amatol p. 362

## CHAPTER XXIV

### SILICA, CLAY, LIME AND GLASS

Silica. Quartz glass. Silicates and silicic acid. Dialysis. Clay. Porcelain, stoneware and earthenware. Mortar and cement. Calcium carbonate. Glass. . . . . p. 381

## CHAPTER XXV

## THE COLLOIDAL STATE

Crystalloids and colloids. Thomas Graham. Heterogeneity of colloidal sols. Adsorption. Precipitation of suspensoids. Emulsoid colloids. Peptisation . . . . . p. 399

## CHAPTER XXVI

## THE RISE OF ORGANIC CHEMISTRY

Organic and inorganic compounds. Isomerism and constitution. Theory of molecular structure. Friedrich August Kekulé. Archibald Scott Couper. Homologous series . . . . . p. 412

## CHAPTER XXVII

## THE ALIPHATIC COMPOUNDS

I. Halogen derivatives. II. Alcohols. Methyl alcohol. Ethyl alcohol. Production of ethyl alcohol. Alcoholic beverages. III. Aldehydes and ketones. Formaldehyde. Acetaldehyde. Acetone. IV. Acids. Acetic acid. V. Ethers and esters. Diethyl ether. Natural fats and oils. Michel Eugène Chevreul. Soap. Soap as a detergent. Hydrogenation of oils. VI. Carbohydrates. Sugars. Starch. Cellulose. Paper. Rayon (artificial silk). Celluloid. Imitation leather and lacquers . . . . . p. 422

## CHAPTER XXVIII

## STEREOCHEMISTRY

Optical activity. Louis Pasteur. Stereochemistry. Theory of van't Hoff and Le Bel . . . . . p. 443

## CHAPTER XXIX

## THE AROMATIC COMPOUNDS

Coal tar. Homology and isomerism. Benzene and its homologues. Phenols. Naphthalene and anthracene . . . . . p. 452

APPENDIX I. List of books for further reading . . . . . p. 458

APPENDIX II. Scales of Temperature . . . . . p. 464

APPENDIX III. The metric system . . . . . p. 465

INDEX . . . . . p. 466

## PORTRAITS AND ILLUSTRATIONS

	PAGE
Early flint arrow-heads . . . . .	14
Flint knife with gold repoussé handle . . . . .	15
ROGER BACON . . . . .	26
"The Alchemist" by A. van Ostade . . . . .	28
A sixteenth-century twin "pelican" . . . . .	29
A sixteenth-century still . . . . .	29
PARACELSUS . . . . .	31
ROBERT BOYLE . . . . .	33
ANTOINE LAURENT LAVOISIER . . . . .	50
JOHN DALTON . . . . .	55
JONS JAKOB BERZELIUS . . . . .	62
DMITRI IVANOWITSCH MENDELÉEFF . . . . .	70
AMEDEO AVOGADRO . . . . .	107
STANISLAO CANNIZZARO . . . . .	134
JOHN MAYOW . . . . .	140
CARL WILHELM SCHEELE . . . . .	147
Scheele's house at Koping . . . . .	148
Priestley's birthplace . . . . .	149
JOSEPH PRIESTLEY . . . . .	150
Priestley's house at Northumberland, Pennsylvania . . . . .	151
HENRY CAVENDISH . . . . .	159
WILLIAM RAMSAY . . . . .	161
Neon lighthouse . . . . .	167
Phosphorus smoke screen produced by a bomb dropped from an aeroplane . . . . .	176
Firing a blast at the Premier Diamond Mine . . . . .	185
Grease plates for retaining diamonds . . . . .	186
Diamond crystal in blue ground . . . . .	187
Graphite furnace in action . . . . .	189
Oil wells near Summerland, California . . . . .	200
Introduction of GAS !! or Throwing a NEW LIGHT on the subject (G. Cruikshank) . . . . .	211
Cutting steel by oxy-acetylene flame . . . . .	219
JACOBUS HENRICUS VAN'T HOFF . . . . .	243
SVANTE AUGUST ARRHENIUS . . . . .	252
HUMPHRY DAVY . . . . .	259
MICHAEL FARADAY . . . . .	262
Faraday lecturing before the Prince Consort at the Royal Institution, December 27, 1855 . . . . .	263
Glauber's furnace for distillation and sublimation . . . . .	277
Knowles' cell for the electrolytic production of hydrogen and oxygen . . . . .	279
Sixteenth-century furnace for smelting iron ores . . . . .	285
Stamps for crushing gold-bearing rock . . . . .	289
Pillar of wrought iron at Delhi . . . . .	295

	PAGE
Tapping a Siemens-Martin steel furnace. . . . .	296
Medal showing tin plague . . . . .	308
Manufacture of white lead . . . . .	311
Molten sulphur being pumped into vat . . . . .	338
Loading sulphur into trucks . . . . .	338
Effect of potash salts on growth of mangolds . . . . .	351
Searles Lake, California . . . . .	352
Chile saltpetre. Emptying the crystallisation tanks . . . . .	356
Effects of inhaling laughing gas (G. Crunkshank) . . . . .	368
Priestley's apparatus for collecting gases over mercury . . . . .	370
Effect of nitrogenous fertilisers (ammonium sulphate) on plant growth . . . . .	374
Rock crystal . . . . .	381
Castle Geyser, Yellowstone Park . . . . .	382
Limestone terraces, Mammoth Hot Springs, Yellowstone Park . . . . .	390
Mediæval glass furnace . . . . .	392
Cylinders of glass produced by the Lubbers process . . . . .	393
Sheet glass produced by the Fourcault process . . . . .	394, 395
THOMAS GRAHAM . . . . .	400
FRIEDRICH AUGUST KEKULÉ . . . . .	416
MICHEL EUGÈNE CHEVREUL . . . . .	433
LOUIS PASTEUR . . . . .	445

# THE SPIRIT OF CHEMISTRY

## CHAPTER I

### THE AIM AND METHOD OF SCIENCE

THE aim of science, it has been said, is to describe truth, and the method of science is the method of discovering truth. But, as "jesting Pilate" asked long ago, What is truth? This is a question which is much more easy to ask than to answer, and fortunately this is no place for a philosophical discussion of the abstract nature of truth. Truth has many aspects. There is a truth in religion, in art and in science, and in each of these domains there are certain accepted criteria of truth, certain tests and methods by which the true may be distinguished from the false. The truth with which science deals is a truth with regard to the external world, the world apprehended by the senses. It is not an unattainable, absolute truth, but a relative or partial truth the nature of which it is not difficult to define, however difficult the truth itself may be of attainment. In the domain of natural science, truth is the coincidence of our conceptions, judgments and propositions with the facts made known to us by means of our senses; and the method of science is the method by which this coincidence is attained and tested. The aim of natural science, then, we may say, is to acquire as complete a knowledge as possible of the material universe; of the objects, materials and phenomena and the relations between the phenomena which make themselves known to us or which we apprehend by means of our senses. Science is objective in its nature and concerns itself only with those facts or experiences which can be observed and verified by all properly trained persons, and with regard to which universal agreement can be obtained. Experiences which are peculiar to an individual, experiences which are subjective in character, form no part of modern natural science. Science, moreover, deals only with recurring or with reproducible phenomena, not with phenomena which are unique.

Throughout all the periods of man's history there must doubtless have been some who became inquisitive concerning the phenomena of nature and the facts of daily experience, and who must have felt an intellectual desire to understand them; but the methods by which it has been sought to attain knowledge, and the tests or criteria of truth by which man's intellectual cravings have been satisfied, have differed greatly.

**The Age of Magic and Mysticism.**- At an early stage of his development, perhaps, man may have learned to appreciate in some measure the beauties of the earth and the glories of the star-lit sky, but, face to face with a universe of great complexity and infinite variety, the intellect was baffled and confused. Overawed by the majesty and power of nature, bewildered by phenomena and experiences which he could not understand, man, in his ignorance, peopled the whole universe with spirits, demons or deities, whom he endowed with human feelings and passions, and to whose benignant or malignant actions all happenings in nature, all good fortune and evil chance for the individual, were attributed. To gain the favour of these spirits or to appease their anger, sacrifices were made; or the evil spirits, to whose presence or actions misfortune or disease were supposed to be due, were made harmless or exorcised by charm, amulet or incantation.

In Chaldea, the priests, watching and recording, generation after generation, the movements of the planets and the aspect of the star-filled sky, accumulated a large amount of definite information and were able even to predict eclipses of the moon; but their minds were obsessed by the idea that the phenomena of nature are subject to the vagaries of supernatural beings and that the stars are the interpreters of the will and desires of the deities. On the stars depended a man's life and actions, his fate and destiny. As Shakespeare makes the Earl of Kent exclaim in *King Lear* :

It is the stars,

The stars above us govern our conditions.

Instead, therefore, of inaugurating a science of astronomy, the priests of Chaldea only built up a superstitious astrology, and occupied themselves largely with divination, sorcery, charm-mongering and the casting of horoscopes. Thereby, no doubt, they acquired much power and influence over men more ignorant and superstitious than themselves.

In Egypt, also, where even 5000 years ago the Egyptian forerunner of Æsculapius, IMHOTEP, had acquired a reputation

for his knowledge of drugs and the treatment of disease, belief in magic retarded the development of medical science. Although, certainly, not a few drugs and remedies of value were known to the priest-physicians of Egypt, their administration could be effective only when the evil spirit to which the malady was due had been driven from the body by incantation and charm. The priest-physician, therefore, had to be "a powerful magician, expert in exorcisms, skilful in manufacturing amulets. Then, with his drugs, he must fight the disorders which the presence of a strange being produces in the body."<sup>1</sup> Egyptian medical practice was thus a curious mixture of magic and medicament, in which incantations and magical hocus-pocus were regarded as being of at least equal importance with the drug.

**Age of Philosophic Enquiry and Speculation.**—To the age of magic and mysticism in which, as we have seen, the existence of mystical and occult forces was assumed in order to explain phenomena apprehended by the senses, there succeeded an age of philosophic enquiry and speculation. In the philosophic epoch of the development of knowledge regarding the material universe, one must recognise the pre-eminence of ancient Greece, where, from the sixth century B.C., with minds freed from the bondage of mysticism and supernaturalism and with a freedom of intellectual outlook hitherto unknown, men sought for a rational and natural explanation of natural phenomena. It was in Greek philosophy that there first arose the idea of cause and effect, of antecedent and consequent, and of arriving at general laws by inductive reasoning. It was in ancient Greece, also, that deductive philosophy first developed and that men first conceived the possibility that truths might be deduced as necessary consequences of some general principle born as the child of imaginative thought. It was the great thinkers of ancient Greece who first formulated most clearly many of the problems which face the modern man of science, and who made the first important attempts at their solution.

Although the early Greek philosophers, who concerned themselves mainly with astronomical phenomena and with such large and general questions as the nature and constitution of matter, based their theories and speculations on observed facts, their views were greatly affected by metaphysical beliefs; and in the later philosophy of PLATO (429–347 B.C.), metaphysics became predominant. For those philosophers the test of truth was self-consistency, and they sought to derive their beliefs from great general principles by a clear and inflexible logic. The

<sup>1</sup> G. Maspero, *Lectures historiques*.

testimony of the senses, even when not ignored as worthless, was but lightly esteemed, and it was held by Plato that knowledge could be obtained "by a simple process of reasoning independently of all information furnished by the senses." Plato, therefore, sought to build up a thought-model of the universe by the exercise of a vigorous imagination and a rigorous logic. That the universe so constructed was often out of harmony with the facts of experience, need occasion no surprise.

Even when the validity of sense impressions and the necessity of building one's beliefs on a foundation of observed fact were recognised and taught by ARISTOTLE (384-322 B.C.), there was no sufficient accumulation of facts on which a sure foundation could be built; and the Greek philosophers did not possess the patience or temperament necessary for the slow collection of facts, nor the means requisite for accurate experimental investigation. Starting from a postulate or premiss based, it might be, on an observation (possibly inaccurate) of fact, or on an analogy (often false), conclusions were reached by logical deduction; but the power of metaphysical views or pre-conceived ideas was strong, and even Aristotle, who insisted on the necessity of careful observation and taught that "more dependence must be placed on facts than on reasonings, which must agree with fact," failed to apply the principles which he himself laid down—principles which form the basis of the modern inductive and experimental method of science—and did not test his conclusions on the touchstone of fact. As Francis Bacon wrote of him: "He had made up his mind beforehand. He did not consult experience in order to make right propositions and axioms, but when he had settled his system to his will, he twisted experience round, and made her bend to his system."

In so far as philosophic views were founded, as many of the Greek views regarding the constitution of matter were founded, on observations of facts, even when the observations were faulty, we need not be surprised that the vigorous imagination and keen intellect of the Greeks should formulate views or theories which find their counterpart in modern scientific doctrine. The Greek philosophers sought, as the modern scientist seeks, to arrive at great generalisations of which individual facts are but parts, and they were the first to lay down some of the principles of modern scientific method. In the circumstances of their times, however, they could not succeed in making any very marked advance in their knowledge of the material universe, and their theories could not but remain to a large extent unfruitful simply because their knowledge of facts was too slight and there was



no possibility of testing the validity of their theories by experiment. Too impatient, perhaps, in their desire to obtain some explanation of the phenomena of nature which would give them intellectual satisfaction, they placed too great an emphasis on imagination and logical reasoning and too little emphasis on experiment and a patient and thoughtful observation of nature. While they understood that Socrates might not greatly advance the science of astronomy merely by "scanning the paths and orbit of the moon, with head thrown back and mouth agape,"<sup>1</sup> they did not, perhaps, sufficiently appreciate the fact that without prolonged and careful star-gazing, accompanied by imagination and logical reasoning, the laws of planetary motion could never be ascertained.

**The Dark and Middle Ages.**—During the Dark Ages which followed on the decay of Greek philosophy and culture in Europe in the sixth century, superstition and a belief in magic and occult forces once more came to life; and even when, with the re-opening of the monastic schools of philosophy by Charlemagne in the eighth century, interest in secular learning began to revive, the power of the Church was predominant. Men's beliefs had now to be brought into harmony with the dogmas of the great ecclesiastical organisation centred in Rome. Scientific study, the study of the material universe, was now bound by the fetters of a particular theology and of a tradition based on the philosophy of Aristotle. Men were not free to study the facts of nature and to reason from them; in any case, they were not free to proclaim the results of their reasoning. And yet, throughout these Middle Ages, when authority was so powerful and when its dictates were imposed with so great severity, there were men who were struggling for intellectual freedom and who were preparing the way for the great spiritual and intellectual re-birth at the Renaissance. The period of the Renaissance, moreover, brought not only a revival of learning but a revitalising of all men's interests and activities, and men set forth in a spirit of high adventure to gain new wealth and to discover new lands and paths across the oceans. No wonder, then, that in the sixteenth and seventeenth centuries great interest and activity in scientific investigation grew up, for the scientific spirit is also a spirit of adventure—of intellectual adventure—a quest of truth which brings a joy and thrill and yields a treasure no less great and satisfying than that of Cabot, which discovered to men the vast continent of the West, or the quest on which Drake sailed in the *Golden Hind*.

<sup>1</sup> Aristophanes, *The Clouds*.

**Modern Scientific Method.**—The founding of the modern scientific method of acquiring a knowledge of the material universe, a method which is based on observation and induction, has often been attributed to FRANCIS BACON<sup>1</sup> (1561–1626), the great thinker, courtier and statesman who in 1618 became Lord Chancellor of England and claimed all knowledge to be his province. Bacon, however, was at most the apostle and missionary of the scientific method who, in his *Novum Organum*, sought to codify the rules of scientific investigation so that all might with equal success add to knowledge. Bacon did not himself engage in scientific investigations, but only “rang a bell to call other wits together.” The origins of the scientific method are to be found in the philosophy of Aristotle, and one of the earliest to put the method in practice was ARCHIMEDES of Syracuse (287–212 B.C.), by whom the foundations of mechanics and hydrostatics were laid. The method has developed gradually and has reached its present state of perfection through the practice of generation after generation of men from the days of Roger Bacon, Leonardo da Vinci and Galileo onwards. Roger Bacon, indeed, who chose as his motto, *Sine experientia nihil sufficienter sciri potest* (“There is no certain way of arriving at any competent knowledge except by experiment”), was one of the earliest to recognise the importance of the experimental and inductive method. In the thirteenth century he wrote: “There are two methods by which we acquire knowledge, argument and experiment. Argument allows us to draw conclusions, and may cause us to admit the conclusions; but it gives no proof, nor does it remove doubt, and cause the mind to rest in conscious possession of truth, unless the truth is discovered by way of experience.” Knowledge of the material universe, then, is to be gained not by argument but by experiment, by inquiry not by disquisition; and this insistence on the importance of facts apprehended by the senses, as the test and criterion of truth regarding the material universe, came as a challenge both to traditional authority and to theological dogma.

*The Collecting of Facts.*—The first step in the building up of knowledge or in the study of a problem by the method of science, is the collecting of facts. These facts are the data supplied by observation of phenomena, either as they occur naturally or as they are produced under conditions controlled artificially by ourselves—that is, by experiment. In chemistry, experiment is predominant, for the conditions under which

<sup>1</sup> Raised to the peerage of England as Baron Verulam and created, at a later date, Viscount St. Albans.

chemical processes, or changes of matter, occur in nature are, for the most part, too complex and obscure to allow of their being unravelled or understood by observation. That iron rusts on exposure to air is a fact of common observation, but it is only by allowing the process to take place under controlled conditions, *e.g.* in presence or absence of moisture, presence or absence of carbonic acid, etc., that it becomes possible to understand the process.

The data of experience, whether they be obtained by observation of natural phenomena or by experiment, must be ascertained as completely, clearly and precisely as possible. Vagueness and indefiniteness cannot be tolerated, for it is on observed facts that the whole structure of scientific knowledge rests; and if the foundations are weak, the building will be untrustworthy and insecure.

It may seem that this first step in scientific knowledge, the accurate ascertainment of facts, is a simple matter; but this is very far from being the case. Knowledge and experience are required in devising the experiments, and manipulative skill and expertness are necessary for carrying them out. Our senses, also, may deceive us, and it is all too easy to miss what may be inconspicuous but important. Temperament and beliefs, moreover, play their part, and one may be led astray by mental bias or preconceived ideas. One is so apt to see what one expects or hopes to see, that truth may be distorted by imagination. The accurate ascertainment of facts, then, requires great honesty of mind as well as prolonged training of hand and eye; and the difficulty of experimental investigation and the liability of all human beings to err, make verification and re-verification of experimental data a necessity.

Accuracy in observation and in the ascertainment of facts has been greatly increased by the invention and perfection of instruments. The introduction of a new, or even the perfection of an old instrument may mark a new stage in the advance of knowledge; and the progress of natural science in modern times is due in great measure to the extension and sensitisation of the human senses by means of instruments. As Humphry Davy said: "Nothing tends so much to the advancement of knowledge as the application of a new instrument. The native intellectual powers of men in different times are not so much the causes of the different success of their labours, as the peculiar nature of the means and artificial resources in their possession."

While the importance of accurate, quantitative measurement in the ascertainment of facts must be recognised, it must also

be borne in mind that all our observations, all our measurements, are subject to error. They can be carried out only with a certain degree of accuracy. We may improve our balances so that a speck of dust suffices to turn the scale,<sup>1</sup> we may aid the eye with microscope or spectroscope, we may increase or strengthen our range of vision so that we may (by inference) count the molecules of a gas and determine the inner structure of a crystal, but in every case there is a certain limit to the accuracy of the measurements. We can know nature only up to a point.

*The Scientific Law.*—While information obtained through the medium of the senses is the foundation, it is only the foundation of scientific knowledge. The collecting of facts is only the first step in the advance of science, for science is not a mere collection of facts, but the satisfaction of an intellectual desire; not a mere gathering of stones along the pathway of life, but the building of these stones into an edifice. Man seeks not only to observe the facts of nature, but to understand them, and one understands them when one knows how the separate facts are related, and when one has learned to see the facts not as separate entities but as parts of a larger whole. After collecting the facts, it is necessary to collate or compare the facts, to classify and arrange them, to separate like from unlike, and to ascertain the relations between the different facts belonging to the same class. The relations so found are then formulated in a general statement, known as a “scientific law” or “law of nature.”

The inductive generalisation of facts—that is, the arguing from particular cases to a general relation—is the second stage in the building of the scientific edifice. Underlying and justifying the whole process of generalisation by induction is the assumption of the uniformity of nature—the assumption, that is, that nature does not behave in a haphazard or capricious way, but that when certain conditions are given, certain results invariably follow. While the uniformity or trustworthiness of nature is, no doubt, an assumption, it is an assumption which is based on and is co-extensive with experience. Formerly, the simplicity of nature was also assumed; but although a law should be stated in as simple a form as possible and should be regarded as simple until the contrary is proved by experiment, the assumption of the simplicity of nature cannot be upheld. As the accuracy of measurement increases, the simplicity of nature generally disappears. The correct formulation of a law in exact

<sup>1</sup> Balances are now in use—so-called micro-balances—by which a difference in weight of one two-hundred-and-fifty-thousandth part of a milligram can be detected.

mathematical terms may become very difficult, but, as the French physicist, Fresnel, wrote : "La nature ne se soucie pas des difficultés analytiques."

It will be clear from what has just been said, that in science the term "law" has a somewhat special meaning. One speaks of a gas, for example, "obeying" Boyle's law, just as one may speak of a person obeying a civil law; but, in science, the term is used only metaphorically. A scientific law does not ordain a certain behaviour; it merely summarises in a general formula a behaviour or relationship which has been observed in a certain number of cases. A scientific law is descriptive, not prescriptive.

A scientific law not only generalises the facts, it also corrects them by smoothing out the irregularities due to experimental error; and it also gives a limited power of prediction. Thus, if the volume of a given mass of air under a given pressure is known, the relevant law (Boyle's law) enables one to predict what will be the volume under any other pressure. It is, however, important to bear in mind that while the prediction may be valid within the range of conditions covered by the experiments, prediction becomes more and more uncertain when it is extended to conditions more and more widely removed from those of the experiments on which the law is based.

*Hypothesis and Theory.*—It is a widespread belief that the aim of science is to "explain" phenomena by ascertaining the cause of effects, and that it is the knowledge of causes that gives intellectual satisfaction. As Vergil wrote long ago,

Felix qui potuit rerum cognoscere causas,

or, in Dryden's translation,

Happy the man who, studying nature's laws,  
Through known effects can trace the secret cause.

This view, doubtless, is correct if one understands aright the meaning of the term "cause." On consideration, we realise that cause and effect mean merely a definite sequence of phenomena under known conditions; they are only links in a chain of processes or phenomena, the cause of one effect being itself the effect of some more remote cause. Cause and effect, in other words, are phenomena which occur in invariable association, and science describes, by means of its laws, the relations between these associated phenomena. It is clear, therefore, that science is concerned only with proximate causes, not with ultimate causes; science describes *how* effects happen and only in a very restricted sense *why* they happen. One *explains* a fact or

phenomenon by showing that it is a particular case of a general law.

Although, doubtless, the structure of scientific knowledge has been built up to some extent by the method of experiment and the use of inductive reasoning based on experiment, the method and aim of science do not consist merely in the "ordering of nature" in descriptive laws. The mind is not satisfied merely by a knowledge of the relations between facts; one must proceed farther and obtain a relation between laws obtain, as one may say, an explanation of the laws and in order to do this it is necessary to add to our knowledge of facts and laws an idea, a conception, an *hypothesis*.

In the development of a science, then, having acquired a basis of knowledge by observation or experiment, and having formulated general laws, one seeks to co ordinate or explain the laws. A guess is made regarding the more fundamental nature of things; not a blind, haphazard guess, but the product of imagination controlled by knowledge and reflection. This guess is called an hypothesis. The hypothesis is not merely a more general and more widely embracing law, based on experiment or sense impressions, but a new conception which is not contained in the facts or data of experience and which passes, indeed, beyond the bounds of possible sense perception. The hypothesis must be in harmony with all the facts as known, and it must be such that the general laws obtained inductively from experiment follow as necessary consequences from the hypothesis. Dalton, for example, sought to explain the laws of chemical combination by introducing the hypothesis that matter is made up of indivisible particles or atoms, that the atoms of a particular element are all alike in their properties but differ from the atoms of other elements. From this hypothesis the laws of chemical combination follow as necessary consequences. Similarly, the various laws of gases are explained by the hypothesis that a gas consists of a large number of small particles, the molecules, and that these molecules are in perpetual and rapid motion, darting about in straight lines and colliding with other molecules and with the walls of the containing vessel.

Having made a guess or invented an hypothesis, one may then proceed according to the logical rules of argument or by the application of known laws, to deduce the behaviour which should be observed in particular cases. This is the *deductive* method of formulating general scientific laws. It is, however, of great importance to bear in mind that these deductive laws must, before they can be accepted into the body of science, be

tested by experiment to find if they are in accordance with fact. In the words of the poet, Alfred Noyes,

naught avails

In Science, till the light you seize from heaven  
Shines through the clear sharp fact beneath your feet.  
This is the test of both—that, in their wedding,  
The light that was a disembodied dream  
Burns through the fact, and makes a lantern of it,  
Transfigures it, confirms it, gives it new  
And deeper meanings ; and itself, in turn,  
Is thereby seen more truly.

When an hypothesis has been found not only to correlate, in a simple and satisfactory manner, known general laws, but when also the deductions are found to be in harmony with fact, the hypothesis takes rank as a *theory*.

It will be clear that by means of hypotheses and deductions from them, the growth of knowledge is made much more rapid than it would be if it were dependent only on inductive generalisation from experiment ; for an hypothesis or theory into which it develops, not only makes it possible to co-ordinate the various known laws—to explain these laws, as we say—but it makes it possible to predict new and undreamt-of laws. A theory not only explains, it predicts ; it not only gives satisfaction to the mind by producing coherence and order among diverse phenomena and the data of experience, but it opens up vistas of new knowledge, suggests new tests of its own validity and spurs one on to fresh adventure. A theory not only illuminates the field of knowledge already explored, but is a torch and beacon lighting up and directing our steps along new paths of scientific discovery.

The progress of scientific discovery and the building up of the edifice of science is thus a process of simplification—simplification by establishing general laws from particular observations, and by the setting up of a theory which co-ordinates and explains these general laws, and much more besides. One must, however, remember that an hypothesis or theory is founded on a basis of facts known at a particular time and that it maintains its validity only so long as it is in harmony with fact. While we may believe that the positive reality of a theory is indicated by its capacity to fit the facts and to constitute, as it were, a model of them, yet we must also bear in mind that a theory rests on an assumption. Although, therefore, our confidence in the truth of a theory increases with increase in the number of laws which it co-ordinates, we must not allow a theory to become a dogma nor the mind to become a bond-slave to it. As know-

ledge increases, a time may come, will almost certainly come, when the new facts no longer fit in with the theory. In some cases, a modification of the original hypothesis may serve to bring the theory into harmony with the new knowledge, but, if not, the hypothesis and theory must be discarded and a new one invented. The history of science can show many examples of discarded theories, theories which were serviceable at one time but which failed to stand the test of the growth of knowledge. Although a theory may become outworn and have to be discarded, the invention of a theory is the most powerful factor in promoting scientific discovery; and even when a theory has ceased to be useful, the facts which have been obtained by its means remain as positive contributions to knowledge. Even on the ruins of a theory one may attain to fuller knowledge, wider outlook and greater power of prediction.

To sum up. In the building up of our knowledge and understanding of the universe, we proceed from carefully observed fact to general law. Imagination then gives us hypotheses and theories which thrill and satisfy the mind by giving to us a wider outlook and fuller understanding of natural phenomena. They explain nature to us by correlating the general laws and by enabling us to fit these laws together, as it were, as part of a general plan, and thereby to construct portions of the edifice of scientific knowledge.

In approaching the study of any branch of science, and not least of chemistry, one must not think of it as a definite body of facts and laws, as knowledge complete and finished, as the last word to be said. On the contrary, as knowledge advances the horizon recedes, and the great theories of science by which we seek to interpret nature and which stand out as among the greatest creative achievements of the human mind, are after all tentative and provisional. Science must rather be thought of as something vital and growing, and as a great adventure in discovery in which all can take, if not an active part, at least a lively and intelligent interest.

**The Classification of the Sciences.**—The great range of scientific study which is co-extensive, as we have seen, with the external universe, and the vast growth of knowledge which has taken place in the past two hundred years, make it impossible for any one to claim, as Bacon did in the seventeenth century, to take all knowledge to be his province. One may, indeed, acquire an acquaintance with a wide range of facts and may take an intelligent interest in many varied aspects of nature, but one cannot become master of more than a small part of



scientific knowledge. To acquire an effective familiarity with and the power of advancing a knowledge of science, it is necessary to limit the range of one's study and effort. A classification or grouping together of the facts and laws relating to different aspects of the external world becomes, therefore, a matter not only of practical convenience but of intellectual necessity. Each group of facts and laws thus formed, together with the relevant hypotheses and theories, constitutes a science or branch of science, and so we speak of the science of chemistry, the science of physics, the sciences of zoology, of botany, and so on.

The subdivision of science, it must be remembered, is not inherent in nature, and our classifications, therefore, are not sharply defined. With the division and subdivision of natural science and the specialisation of study which the enormous growth of knowledge has brought about, it is important not to lose sight of the unity of nature and to recognise that although each branch of science has a certain individual and distinctive character, it does not stand isolated from and independent of other branches. Knowledge is constantly bursting the barriers of our classifications, and the truth found in one science may irradiate the problems of another.

As a matter of convenience and to facilitate the advance of knowledge, it is customary to classify the main branches of natural science into the two large groups :

- I. The Physical Sciences, *e.g.* physics, chemistry, geology.
- II. The Biological Sciences, *e.g.* zoology, botany, physiology.

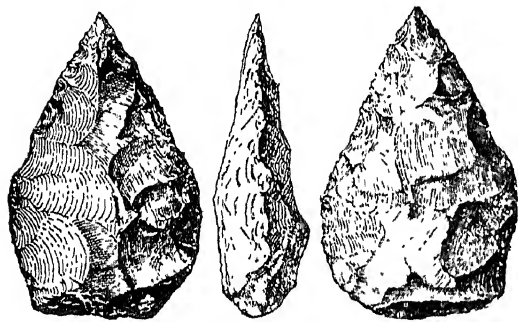
In the latter group of sciences, one studies the behaviour of matter in its association with life and the phenomena which are observed in the living animal or vegetable organism ; whereas, in the former group, one studies the properties of inanimate matter or the properties of matter apart from life.

## CHAPTER II

### THE TWILIGHT AGE OF CHEMISTRY

ALTHOUGH chemistry as a science is of comparatively recent origin and extends no farther back than the time of Robert Boyle in the middle of the seventeenth century, a consciousness of the variety of materials occurring on the earth is doubtless coeval with man's existence.

**Prehistorical Development.** During the long and uncertain twilight of more than half a million years which preceded the emergence of man as a fully erect, reasoning and forethinking animal, man's forerunners were preoccupied mainly with the



Early flint arrow-heads.

(From J. de Morgan's *Pre-historic Man*.)

obtaining of food and with self defence against the mammoth, the woolly rhinoceros, the sabre tooth tiger, the bear and other animals which roamed the world with them. No doubt, as Lucretius wrote : " Arms of old were hands, nails and teeth, and stones and boughs broken off from the forests, and flame and

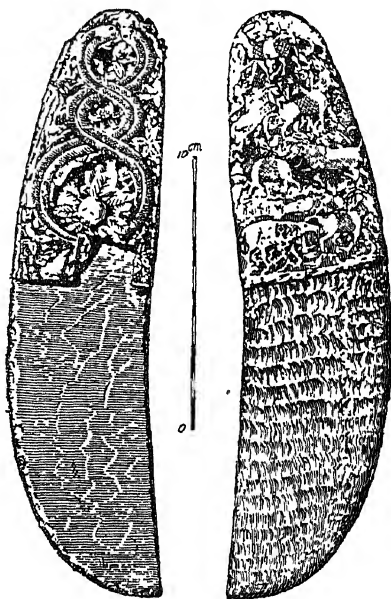
fire, as soon as they had become known " ; but the early sub-men soon learned that they could make their stone clubs more effective by breaking them off to a sharp edge, and that they could improve their wooden staves by grinding or burning their ends or by tipping them with a sharp piece of flint or of bone. It is impossible to say when these primeval men learned that flint could be chipped into flakes or fashioned into sharp-cutting axes and knives or pointed spearheads, but it must have been at a very early time ; and chipped flints are among the earliest records known of man or a man-like animal. For many thousands of years, right down into historical times, man's most important

implements and weapons were made of flint, of obsidianite (a volcanic glass), or other stone, fashioned and polished, as time went on, with ever greater expertness and refinement.

With the coming of true man (essentially as he exists at the present time), perhaps some thirty or forty thousand years ago, a higher civilisation, greater culture and social organisation began to develop, and a wider range of materials came into use. Man now found shelter, not in forests or under rocks, but in caves, the walls of which he adorned with drawings of animals, still to be seen in the caves in France and Spain. As pigments he used iron ores or ferruginous clay (which gave red, chocolate, orange and yellow colours), charcoal and pyrolusite (black), and kaolin (white), mixed with fat; and to illumine his dark abode, the early cave-man used lamps of which the container was probably a hollow bone, or shell, or shallow dish of soap-stone. The fuel was bone marrow or animal fat, and the wick, moss. Although during man's earliest years only a comparatively small number of materials would be known and made use of, yet throughout the long succeeding ages, knowledge would gradually grow and man would learn, at first by accident and later by conscious effort, how the naturally occurring materials

could be altered and new materials produced from them. Doubtless the growth of knowledge was slow, but the time was very long, and one need not therefore be surprised that even the earliest historical records left by man, bear testimony to the existence of an extensive knowledge of diverse materials, and to an already highly developed civilisation.

**Ancient Chemical Knowledge.**—Whether the early culture from which the Western civilisation of the present day has developed, was born among the Sumerian tribes of the Tigris and Euphrates valleys, or among the dwellers in the valley of the Nile, is perhaps open to doubt; but it was cradled in the



Flint knife with gold-leaf repoussé handle.

(From J. de Morgan's *Pre-historic Man*.)

basin of the Mediterranean, and it is in Egypt that the early records of our civilisation have been most clearly and most abundantly preserved. The practice of the arts of chemistry, *i.e.* the arts of transforming materials, spread to all the nations of antiquity—the Egyptians, Chaldeans, Hindus and Chinese—as they slowly advanced towards a more highly developed civilisation, but by none were the operations of chemistry carried out more extensively than by the Egyptians. It is, indeed, to the pre-eminence of ancient Egypt in the practice of chemical operations that we owe, most probably, the term “chemistry,” a word which is derived, as it is thought, from *Chemī* (meaning black), the ancient name given to Egypt on account of the dark colour of its soil.<sup>1</sup>

The materials known to and used by the ancients were numerous, and many diverse operations of a chemical character were carried out. Many naturally occurring minerals, such as agate, amethyst, beryl, carnelian, lapis lazuli and turquoise, were used as ornamental stones or as amulets and charms. Other minerals, of which one may mention the oxides of iron, copper and manganese, various ferruginous clays, cinnabar (sulphide of mercury), malachite (copper carbonate) and chrysocolla (copper silicate), were used as pigments. Galena (sulphide of lead), and to a less extent “stibium” (sulphide of antimony), were used in Egypt from very early times, for darkening the eye brows and eyelashes; and ground malachite, similarly, found application even among the pre-dynastic Egyptians of the fourth millennium B.C., as a cosmetic. With this material the Egyptians painted the eyes in order, it is supposed, to protect them from the glare of the sun and the attack of flies.

Among the most important of the ancient arts and crafts, the beginnings of which are lost in the mists of pre history, are those of extracting and working metals. Gold, which occurs native, may possibly have been the first metal to be discovered, but even copper and lead, which must be extracted from their ores, were known in Egypt in pre-dynastic times; and during the three or four thousand years which preceded the beginning of the Christian era, men also became acquainted with silver, iron, tin and mercury, and with the alloys electrum (alloy of

<sup>1</sup> It is stated by authorities that the word *χημία* (*chemia*) or *χημεία* (*chemeia*) probably first occurs in a decree, issued by the Emperor Diocletian towards the end of the third century, ordering the destruction of all books dealing with *chemia*, or the preparation of silver and gold. Later Byzantine writers used the word *χυμεία* (*chymeia*), which is regarded as falsely derived from *χυμός* (*chymos*) “liquid. In this we may see the origin of the old English form, *chymistry*. Derived from *Chemī*, Chemistry would mean the Egyptian Art or, as it was later called, the Black Art.

gold and silver), bronze and brass. Even as early as the fourth century B.C. craftsmen of Damascus were damascening steel as well as weaving fine linen.

The discovery of alcoholic liquors and a knowledge of the process of fermentation date back to some unknown period prior to 2000 B.C. At first men brewed mead from wild honey and a beer from red barley, similar, doubtless, to the "kaffir beer" made for ages and even at the present day by the natives of South Africa from millet; but later, as is recorded of Noah, men "planted a vineyard and drank of the wine." Even as early as 1600 B.C., much wine was produced in Syria and in Hebron; and Helbon (Chalybon), whence the kings of Persia obtained their supplies, early became noted for the excellence of its vintage.

At a very early period the Egyptians became acquainted with the manufacture of leather, which they used as coverings for stools and chairs as well as for beds and cushions. The Egyptians, also, discovered how to manufacture faience, glass and enamel, and were expert in the art of dyeing and the use of mordants.

To those accustomed to the great variety of shade and colour which is a feature of present-day Western civilisation, and which is made possible by the production of innumerable dyes derived from the constituents of coal tar, even Joseph's coat of many colours would appear a crude and commonplace affair. For although the dyers of the ancient world were able, by mixing the dyes, to produce variation in shade, yet the number of dyes at their disposal was comparatively small. At first, dyes derived from plants were used, and of these the earliest known was probably indigo, obtained from various species of *Indigofera*, and produced mainly in India. This dye, renowned for its fastness, has been detected on mummy-cloths dating back to 5000 years ago. Alizarin, a red dye obtained from the root of the madder, and a yellow dye extracted from the Safflower (*Carthamus tinctorius*), were also in use at a very early period.

At a later time, more especially in Syria, dyes of animal origin were discovered and introduced. Of these the best known were the scarlet dye kermes,<sup>1</sup> obtained from the bodies of the insect kermes—an insect akin to the Mexican cochineal—and Tyrian Purple or the Purple of the Ancients, the most costly dye of the ancient world, the "dye of dyes,"

Whercof one drop worked miracles,  
And coloured like Astarte's eyes  
Raw silk the merchant sells.

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<sup>1</sup> From which are derived the words carmine and crimson.

This dye, which is formed when a secretion of certain shellfish, more especially *Murex brandaris* and *Purpura lannastroma*, is exposed to sunlight, was first manufactured at Tyre and later at many other places on the shores of the Mediterranean. It was rediscovered in Ireland in the seventeenth century.

Fragrant resins, spices and balsams (frankincense and myrrh, cinnamon, cassia and others), for use as incense, the preparation of cosmetics and the mummification of the dead, were much employed and formed an important part of the early commerce of the Eastern peoples.

Surrounded as they were by many plants in which were formed compounds possessing a marked physiological action, it is not to be wondered at that the peoples of Egypt, India and China early became acquainted, perhaps through painful experience, with the baneful action or with the medicinal or curative value of certain plants. This knowledge grew with the years, and in the temple-laboratories of Egypt, the priest physicians extracted the vegetable oils and alkaloids, and compounded their drugs and love potions. Thus we learn that castor oil was a household remedy among the Egyptians even four thousand years ago, and henbane (*Hyoscyamus*) was used to relieve pain in cases of dental caries. Mandragora (mandrake) root, moreover, was used not only as an aphrodisiac to bind the affections of a wayward lover, but also to produce narcosis in surgical operations. The narcotic properties, indeed, of many plant products were known at an early date, and it was doubtless with a preparation of Egyptian opium, or it may be hemp, that Helen, as is recounted in the Homeric poem, sought to bring forgetfulness of their sorrows and sufferings to Telemachus and Menelaus :

And Helen of birth divine took thought in the selfsame hour,  
And she mingled along with the wine a drug of marvellous power :  
Sorrow and wrath by the draught and cares shall be swept from the soul,  
If a man of the cup shall have quaffed when this hath been cast in the bowl.  
No tear for the rest of the day shall adown on his cheeks be shed,  
No, not if before him lay his father and mother dead,  
Not even if full in his view his brother or darling son  
With the pitiless sword they slew, and he looked with his eyes thereon.  
Such drugs of might, I ween, unto Helen the fair were known,  
Given unto her by a queen, Polydamna the wife of Thôn,  
Of the land of Egypt, where from the corn-giving earth drugs spring :  
Great store of the good doth it bear, and many an evil thing.<sup>1</sup>

Although the Egyptians acquired, in the various craft guilds which developed in association with their religious temples, great skill and expertness in divers arts and crafts (glass, pottery,

<sup>1</sup> *Odyssey*, Book IV. Translation by A. S. Way.

enamel and metal work, tanning and dyeing, etc.), and accumulated a considerable store of knowledge relating to drugs, vegetable oils and balsams, they possessed, apparently, but little curiosity regarding the nature of the numerous processes of a chemical character which they carried out. The Egyptians were pre-eminently a practical people and felt no urge to pursue truth for truth's sake; rather were they eager to increase the comfort and improve the amenities of everyday life. There is no evidence of the existence in ancient Egypt of the spirit of philosophic enquiry such as arose in India, in Chaldea and in Greece. On the contrary, the chemists (if so one may call them) of Egypt were artificers, not philosophers; craftsmen, not men of science.

**Greek Philosophy.**—While the Egyptians were practical in their outlook and empiricist in their development of knowledge, the temperament of the ancient Greeks was idealistic and philosophic. It was not, however, in unravelling the nature of the minor processes of chemical change that the Greek thinkers were interested; they preferred to allow their imagination to play around the great problems of the origin of the universe and the ultimate constitution of matter. Men of other races, certainly, had speculated on these great problems, but it was in Greece that the streams of thought flowing from other countries, more especially from India and Chaldea, mingled and became clarified; and it was by the philosophers of Greece that new paths of advance were opened up for others more fitted to travel along them.

Into the ancient speculations regarding the constitution of matter, the philosophers belonging to the Ionian School introduced the great simplifying conception of a single *prima materia* or universal principle underlying all forms of matter, a simplification towards which modern science has been laboriously striving for the past hundred years. To THALES, in the seventh century B.C., the *prima materia* was water; to ANAXIMENES, in the sixth century, it was air, both these things being, according to common observation, all-pervading and essential to life. From water or from air, all things were supposed to proceed by a process of rarefaction or of condensation.

Into the philosophy of the Ionian School, PYTHAGORAS, in the middle of the sixth century, introduced the conception of number and of order. The diverse forms of matter are not produced from primitive matter in any haphazard fashion, but according to number, according to harmony. Law and order prevail. The idea of discontinuity of matter was also introduced.

While retaining the Ionian conception of a single, fundamental unity underlying all matter, HERACLITUS of Ephesus, in the sixth century, introduced the idea of motion, of mobility, of change, as exemplified in a visible form by fire. To Heraclitus, all matter is in a state of flux—his views being summed up in the well-known dictum, *πάντα ῥεῖ* (*panta rhei*). "Change is everywhere, everything is and is not; there is no stability. Even in the same river one cannot bathe twice, nor even once." The idea of the continuous motion of particles is at the basis of the modern kinetic theory of matter.

From the observation that when wood is burned flame or fire is produced, that smoke or air ascends, that moisture escapes and can be condensed to water, and that ash or "earth" remains as a residue, EMPEDOCLES, in the fifth century B.C., regarded fire, air, earth and water as the four primary, elementary constituents of matter. From these four eternal, indestructible and immutable elements, all known forms of matter were regarded as being produced by combination (under the influence of "love"), or by separation (under the influence of "hate"). This view of the four elements is of particular interest because, modified a century later by Aristotle, it dominated philosophic and scientific thought until the time of Robert Boyle in the seventeenth century; and the idea lingers on in the everyday language of the present day.

In the philosophy of ARISTOTLE (384-322 B.C.) there was first added to the four elements of Empedocles, a fifth, *æther*, which soon, indeed, absorbed the other four and became the one primordial quintessence of matter which acted as the carrier of the four essential properties or qualities, hotness, coldness, dryness, wetness; and the combination of these properties, in pairs, was supposed to give rise to the four primary forms of matter—fire (hot and dry), air (hot and wet), earth (cold and dry), water (cold and wet). By the union of these qualities in different proportions, the diverse kinds of matter were supposed to be formed. So long as this view obtained, that matter has no reality in itself but is merely the carrier or embodiment of certain qualities, it is clear that the conversion of one form of matter into another by altering the proportions of the elemental qualities, would appear to be quite feasible; and the aim of the ancient and mediæval alchemists, therefore, to effect such a transmutation would seem to be neither hopeless nor absurd.

Underlying the philosophy of Aristotle, and most of the other Greek philosophies, is the idea that matter is continuous; that



it is capable of infinite subdivision. But we must now turn to the essentially different view, put forward in the fifth and fourth centuries B.C., by LEUCIPPUS, DEMOCRITUS and EPICURUS. According to the doctrine of these philosophers, a doctrine which comes nearer to modern scientific views than any other system of philosophy of the ancient world, and which has been preserved and expounded by the Roman poet LUCRETIVUS (98-55 B.C.), "matter does not cohere inseparably massed together," but is made up of individual particles, the "atoms" or the "first-beginnings of things," which are immutable and eternal. These "first-beginnings" are in constant motion, travelling through void. As Lucretius writes: "Since this then is a certain truth, sure enough no rest is given to first bodies throughout the unfathomable void." "Of this truth which I am telling we have a representation and picture always going on before our eyes and present to us: observe whenever the rays are let in and pour the sunlight through the dark chambers of houses, you will see many minute bodies in many ways through the apparent void mingle in the midst of the light of the rays, and as in never-ending conflict skirmish and give battle, combating in troops and never halting, driven about in frequent meetings and partings, so that you may guess from this what it is for first-beginnings of things to be ever tossing about in the great void." The first-beginnings were not regarded as being all alike but as differing in size and shape and compactness. By the coming together and coherence of these atoms, the diverse substances are formed; and the diversity of substances was regarded as being due, not to differences in the nature of the atoms, but to differences in their size and shape and manner of their union. As explained by Lucretius: "Now mark and next in order apprehend of what kind and how widely differing in their forms are the beginnings of all things, how varied by manifold diversities of shape; . . . the things which are able to affect the senses pleasantly, consist of smooth and round elements; while all those on the other hand which are found to be bitter and harsh, are held in connexion by particles that are more hooked and for this reason are wont to tear open passages into our senses and in entering in to break through the body. . . . Again, things which look to us hard and dense must consist of particles more hooked together, and be held in union because compacted throughout with branch-like elements."<sup>1</sup>

**Rise and Development of Alchemy.**—While the ancient Egyptians accumulated, over a long period of time, a great

<sup>1</sup> Lucretius, *de rerum natura*, translation by Munro.

store of facts relating, more especially, to drugs and metals, their knowledge was purely empirical. They did not seek for, or in any case they did not obtain, any real understanding of the processes they carried out, or any general laws binding together the isolated data of experience. No attempt was made to classify phenomena, and practice was without the guidance of theory. Among the Greek philosophers, on the other hand, theory was divorced from practice, and although imagination supplied a wealth of theories, these theories lacked an adequate foundation of experimental fact and were incapable of experimental verification. In Alexandria, however, which in the third century before the Christian era had become the centre of Hellenistic culture, Egyptian technical knowledge became united with Greek philosophic speculation, and from the union there arose the first crude beginnings of a science of chemistry.

In the great temple-laboratories of Egypt, as we learn from a papyrus of workshop receipts discovered early last century at Thebes, Egyptian craftsmen had achieved much success in the production of alloys and in superficially colouring the baser metals so as to counterfeit the appearance of gold and silver. These craftsmen, however, had no illusions regarding their work and held no mistaken idea of transmutation; nor had they, we may suppose, any greater intention to deceive than have their successors at the present day who produce and put on the market various metallic alloys resembling the noble metals in appearance.<sup>1</sup> Their purpose was to supply those who did not care to pay the price of the genuine article with cheaper substitutes of similar appearance; and the industry apparently became a profitable one, for, as Pliny wrote,<sup>2</sup> the art of making alloys "formerly done for the sake of reputation, is now undertaken for the mere purpose of gain . . . men of rank in all countries endeavoured to acquire fame by the practice of it."

Following on the proscription of the Egyptian religion, the destruction of the temples and the burning of the great libraries of Alexandria by the Roman emperors, there was formed among

<sup>1</sup> Practical men were able to distinguish between gold and alloys and even to evaluate the "fineness" of gold alloys by the colour and nature of the streak on touchstone (a velvet-black silicious stone or flinty jasper), and also by the specific gravity, as we know from the story of Archimedes and King Hiero's crown. At an early time, also, gold was tested by heat. Thus, in one of the Tell-el-Amarna letters, Buraburias, king of Karadunias, wrote to Amenophis IV, king of Egypt, in reference to a gift of gold which the latter had sent, "the . . . minas of gold which they brought me, when I put them in the furnace, they were (undervalue), not of full weight."

<sup>2</sup> *Natural History*, 34, 3.

the scattered priesthood a secret cult in which the technical knowledge of the Egyptians was mixed with the philosophic doctrines of Plato and Aristotle and the mysticism of Persia and Chaldea. Under the intellectual domination of the Aristotelian doctrine that the material universe is made up of one primordial matter which acts as the carrier of certain essential properties, the view readily arose that the conversion or transmutation of one kind of matter into another might be brought about by altering the proportions of the essential qualities. In minds attuned to such a doctrine, the fact that alloys resembling gold in appearance can be produced from baser metals, that silver is found occurring in lead ores, etc., gave rise to the view that actual transmutation—partial or complete—had taken place. Such a secret and mystical cult, which claimed as its divine founder HERMES TRISMEGISTOS,<sup>1</sup> the “thrice-great Hermes” (identified with the Egyptian god Thoth), and which surrounded itself with an air of mystery and imparted its secret knowledge only to the initiated, readily became a prey to obscurantism, necromancy and magic. When, therefore, the Roman Emperor Diocletian, in A.D. 292, ordered the destruction of all books dealing with *chemia* or the art of making gold and silver, he may have been moved thereto not merely by a fear that the currency would be debased but, as Gibbon suggests,<sup>2</sup> because he “was desirous of preserving the reason and fortunes of his subjects from the mischievous pursuit.”

Of the state of chemical knowledge in the third century and the mental outlook of those who sought to practice transmutation, a picture is given to us in the works of ZOSIMOS of Panopolis, who lived about A.D. 300. In these works, which exercised a considerable influence on, and were frequently quoted by, later writers, there are given many laboratory receipts and directions, often couched in mystical language unintelligible to all but, presumably, the initiated adepts, as well as descriptions of furnaces, stills (Fig. 1) and other apparatus then in use. For success in the art, we learn, a man must be pure in mind and free from avarice, and the planets also must be favourable.

When the Museum of Alexandria and the last of the schools of science and philosophy were closed in A.D. 415, many scholars, carrying with them a knowledge of and interest in the ancient learning, fled to Syria and Persia. There they translated into Syrian many Greek and Græco-Egyptian works dealing with

<sup>1</sup> From this mythological founder are derived the terms “hermetic art” and “to seal hermetically.”

<sup>2</sup> *Decline and Fall of the Roman Empire*, Chap. 13.

philosophy, medicine and technical arts. After the conquest of Persia, Syria, and Egypt by the Arabs, following on the rise of Islam in the seventh century, these Persian and Syrian scholars were held in high esteem, and were welcomed at the courts of

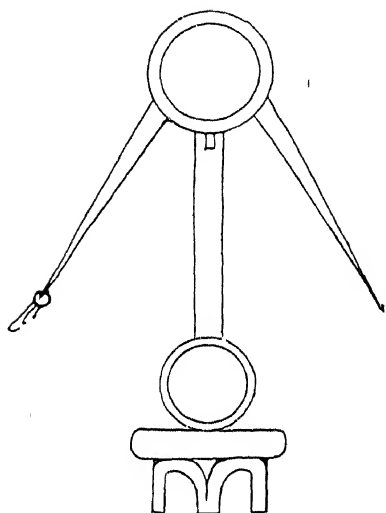


FIG. 1.--Early apparatus for distillation.

The vapour from the boiling liquid is condensed in the upper flask, and the liquid formed escapes through the side tubes.

when chemistry became an exact science. During that period chemical science was dominated mainly by the philosophy of Aristotle and a belief in the transmutability of metals.

When the ancient knowledge passed under the care of the Arabs, much of the mysticism and obscurity which had characterised the chemistry of the Alexandrian school was swept away; and the investigation of "the properties and generation<sup>2</sup> of minerals and of substances obtained from animals and plants," was undertaken in a more systematic and scientific manner. This new direction of thought and investigation is first clearly found in the works of JABIR IBN HAYYAN (721-813), generally known to the West as GEBER, a Persian by birth who came to occupy a position of much influence and importance at the court

<sup>1</sup> This applies, of course, only to the material side of alchemy. The mystical side of alchemy does not concern us here.

<sup>2</sup> It was supposed that metals, for example, were generated in the earth, in analogy with the generation of animals.

such caliphs as Harun al Rashid, who reigned from 786 to 809. Translations of the ancient works into Arabic were now made, and although the Arabs did not themselves add greatly to the older knowledge, they became its guardians during the years when Western Europe was suffering martyrdom and was being ravaged by the Goths, the Vandals and the Huns. To the term *chemia* of Hellenistic culture, the Arabs prefixed their definite article, and so gave us *alchemy*, a term which, although not differing in its signification from chemistry,<sup>1</sup> it is convenient to apply to that period of chemical study and investigation which developed mainly under the influence of the Arabs, and which lasted down to the seventeenth or eighteenth century

of the renowned caliph Harun al-Rashid towards the end of the eighth century. Geber devoted himself eagerly to experimental investigation and accomplished not a little towards laying a solid foundation for future science. At that time, and for long afterwards, the commonest operations of the alchemists were *calcination*, more especially of metals, for the purpose of removing impurities, *sublimation* and *distillation*, and a clear account of these is given by Geber. Geber also devoted himself to the development of a number of the practical applications of chemistry.

In the works of Geber, also, we find expressed the view—derived perhaps from an earlier period—that “all metals are in their essences mercury coagulated with sulphur . . . and they differ only on account of their different ‘accidental qualities.’” By “mercury” and “sulphur” were meant not the substances known to us by these names but hypothetical substances which are a sort of quintessence of the common substances. “Mercury” conferred the property of fusibility, malleability and lustre, while to “sulphur” was due the property of combustibility or alterability by fire. The differences which exist between metals were supposed to be due to differences in the relative proportions of “sulphur” and “mercury” in them; and, on this view, therefore, by altering these relative proportions it should be possible to transmute one metal into another.

Although most of the Arabian alchemists were believers in the possibility of transmutation, there was one notable exception, namely, the philosopher, poet and physician, “the Hippocrates and the Aristotle of the Arabians,” IBN SINA or AVICENNA (980–1037), who held that it is no more possible to transmute silver into gold or copper into silver than it is to convert a horse into a dog or a man into a bird.

With the conquest of Spain by the Moors in the eighth century and the founding of a university at Cordova which attracted scholars from England, France and Germany, the Arabian learning was introduced into Western Europe. Through the translations of Arabic works by the Englishman ROBERT OF CIESTER in 1144 and others, a knowledge of alchemy was spread abroad, and not only the intellectual interests but also the cupidity and avarice of many were thereby stimulated and inflamed. In Europe, alchemy, finding a soil very favourable to its growth, took firm root, and during the twelfth and thirteenth centuries, more especially, and also long afterwards, flourished luxuriantly, the main object of endeavour being the discovery

of the "Philosopher's Stone,"<sup>1</sup> by means of which base metals might be transmuted into gold.

To some, probably, of the greatest scholars, like the great Dominican monk and Bishop of Regensburg, ALBERTUS MAGNUS<sup>2</sup> (1193-1282), the "Doctor Universalis" *magnus in magia naturali, maior in philosophia, maximus in theologia* and the English Franciscan Friar, ROGER BACON (1214-1292) - the



ROGER BACON.

"Doctor Mirabilis"—the theory of a *prima materia* and the conception of transmutation made chiefly an intellectual and philosophic appeal. The former, certainly, did not believe in the actuality of transmutation, for he wrote: "Alchemy cannot change metals but can only imitate them. . . . I have tested alchemistic gold. After six or seven heatings, it is burned and reduced to ashes."<sup>3</sup> In the *Speculum Alchemiæ* or *Mirror of Alchemy*, a work usually attributed to him, Bacon writes:

<sup>1</sup> This was also called by many other names, such as, the elixir, the magisterium, the stone of wisdom, etc.

<sup>2</sup> His true name was Albert von Bollstädt.

<sup>3</sup> *de mineralibus*, Book 3, 9.

"Another [besides Hermes] has said: Alchemy is a science which teaches how to transform any kind of metal into another: and this by a suitable medicine, as is made clear in many books of the Philosophers. Wherefore, alchemy is a science which teaches how to make and prepare a certain medicine, called an Elixir, which when thrown on metals or imperfect bodies, doth in the moment of the projection make them completely perfect." Of the production of metals in the earth, he writes: "It is to be noted that the mineral principles in the mines are mercury and sulphur. From these, all metals and all minerals, of which there are many and diverse kinds, are generated. But I say that nature always aimed at and strove to achieve the perfection of gold. Diverse accidents, however, supervening, transform the metals, as is found stated sufficiently clearly in many books of the Philosophers."

In the *Mirror of Alchemy*, Bacon is not so much expressing his own views as attempting to give a clear account of the views and beliefs of the "Philosophers" as set forth, often obscurely and in riddles, by the Arabian writers.<sup>1</sup> It may be that Bacon accepted these views and beliefs, but there is little evidence that he busied himself in the practical tasks of achieving transmutation. Although Bacon could not free himself entirely from the fetters of authority and dogma and from the prejudices of his time, it should be remembered that he was one of the first to insist on and to practise the experimental and inductive method of science, the method by which the fetters of authority, prejudice and superstition were ultimately broken.

Of the alchemists who accepted the doctrine of the transmutation of metals, many, doubtless, were imbued with the honest and single-minded desire to learn the secrets of nature; and they devoted themselves—under the guidance of an erroneous theory—with an intense and feverish activity, to the practical task of finding the "Philosopher's Stone" and of effecting actual transmutation. "They are not given to idleness," wrote Paracelsus, "nor go in a proud habit, or plush and velvet garments, often showing their rings on their fingers, or wearing swords with silver hilts by their sides, or fine and gay gloves on their hands; but diligently follow their labours, sweating whole days and nights by their furnaces. They do not spend

<sup>1</sup> The view that "mercury" and "sulphur" are the underlying principles of all metals, and that the production of the perfect metal, gold, is the end and aim of nature's striving—a process which may be accelerated by means of the "philosopher's stone"—is found in the works of Jabir or Geber. Subtle, in Ben Jonson's play, *The Alchemist*, expresses the current alchemistic belief in the words: "Lead and other metals . . . would be gold if they had time."

their time abroad for recreation, but take delight in their laboratories. They put their fingers among coals, into clay and filth, not into gold rings. They are sooty and black, like smiths and miners, and do not pride themselves upon clean and beautiful faces."

In the search for the philosopher's stone, all the kingdoms of nature—animal, vegetable and mineral<sup>1</sup> were ransacked,



THE ALCHEMIST.

After a painting by A. van Ostade (1661).

(National Gallery, London.)

On the sheet of paper lying on the floor the artist, with ironic humour, has painted the words, *oleum et operam perdis, thou labourest in vain.*

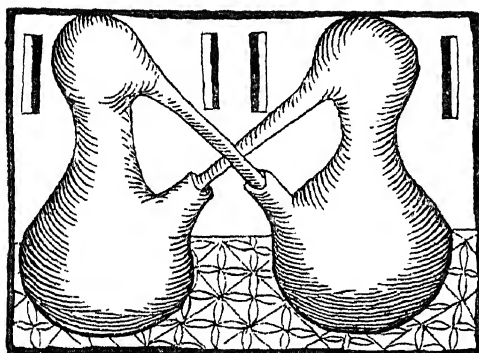
and minerals of all kinds, plant juices and animal secretions and excretions, were calcined, fused, boiled and distilled. Some of these alchemists undoubtedly believed that they had discovered the Philosopher's Stone and had actually accomplished transmutation.

If, however, there were some alchemists who were honestly striving after knowledge, there were also many for whom avarice and cupidity were the loadstars, and it is they who have caused

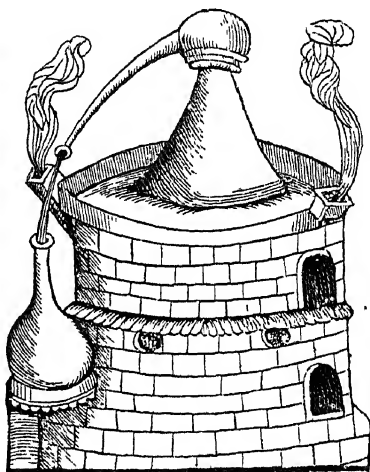
<sup>1</sup> This classification we owe to the Arabs.



alchemy to be associated in men's minds with deceit, quackery and charlatanism. "The darkness of the middle ages ensured a favourable reception to every tale of wonder, and the revival of learning gave new vigour to hope, and suggested more specious arts of deception";<sup>1</sup> and for hundreds of years the conviction that gold could be produced by the transmutation of the baser metals was widely and firmly held in Europe, not only by the ignorant but even by the learned, and by kings, rulers and governments who, seeking to fill their coffers with alchemistic gold, only succeeded in falsifying and depreciating their currency.



A sixteenth-century twin "pelican" or circulatory vessel, for the prolonged heating of liquids.



A sixteenth-century still.

As time went on the boasts of the alchemists became more extravagant—"I could change the whole sea into gold if it were mercury," asserted RAYMOND LULLY—and it was also claimed for the Philosopher's Stone not only that it would produce gold but that by it "all infirmities may be cured, human life prolonged to its utmost limit, and mankind preserved in health and strength of body and mind, clearness and vigour."<sup>2</sup>

If the alchemists of the middle ages failed in their endeavour to transmute the baser metals into gold, they and the many unlearned craftsmen who for centuries carried on their avocations and ministered to the needs of their fellow-men, prepared a large number of new and important substances (the mineral acids, for example), obtained greater knowledge of many chemical pro-

<sup>1</sup> Gibbon, *Decline and Fall of the Roman Empire*, Chap. 13.

<sup>2</sup> Report of a Commission to Henry VI of England. See Traill, *Social England*, 2, 374.

cesses and perfected apparatus and methods of work. During the alchemistic period, therefore, a broad foundation of knowledge was being prepared on which the future science might be built. As Francis Bacon wrote: "Alchemy may be compared to the man who told his sons that he had left them gold buried somewhere in his vineyard; where they by digging found no gold, but by turning up the mould about the roots of the vines, procured a plentiful vintage." The daughter, it may be, of error, alchemy became the mother of knowledge and truth.

The belief in the transmutation of metals, although it persisted till the eighteenth century, had long been waning in vigour as men became more conscious of its failures and as the true spirit of scientific investigation slowly developed. In the sixteenth century, moreover, alchemy acquired a nobler aim and ideal under the influence of PARACELSUS (1493-1541), who taught that the true aim of alchemy is the curing of human illness and disease, and that the preparation of drugs is the main object of the chemist. A new era in chemistry was thereby inaugurated, known as the period of *iatrochemistry*,<sup>1</sup> or medical chemistry.

PHILIPPUS AUREOLUS THEOPHRASTUS BOMBASTUS VON HOHENHEIM, commonly called PARACELSUS, one of the outstanding figures of the sixteenth century, was a man of genius and of great sincerity but possessed of a restless and turbulent spirit. Self-sufficing and defiant, he was by temperament a reformer and a rebel against convention and authority. Born at Einsiedeln, in Switzerland, in 1493, he took up the study of medicine and, after much wandering and a varied experience, became City Physician and Professor of Medicine in the University of Basle in 1526.

Speaking in German instead of in Latin, the language at that time of the universities, Paracelsus, even in his opening lecture, made public declaration of his opposition to accepted medical authorities, and melodramatically consigned to the flames the works of the older writers, Galen and Avicenna, with whose teaching he disagreed. Thereby, perhaps, he was copying the action of another great reformer, Martin Luther, who, six years before, in the presence of an assembled multitude of doctors, students and citizens, had publicly burned the papal bull of anathema at the Elster Gate of Wittenberg.

The aggressive disposition of Paracelsus and his unorthodox beliefs soon led him into conflict with his colleagues and the civic authorities. Within a year, he abandoned his official

<sup>1</sup> From *ιατρός* (*iatros*), a physician.

positions, and, becoming once more a wanderer seeking and urging others to seek knowledge not from books but from contact with reality, he passed from place to place, teaching his new doctrines and spreading abroad a knowledge of them by means of his writings. He died at Salzburg, in Austria, in 1541.

Extending the theory of Geber, Paracelsus adopted the view that all matter is made up of three elements or principles, *tria*



PARACELSUS.

After a Painting by J. van Scorel  
(The Louvre, Paris.)

*prima*, "mercury," "sulphur" and "salt," the last-mentioned representing the principle of unchangeability by fire. "When these three are combined then we have what we call a body, and nothing is added to them except life and what depends upon it." Diseases he considered as being due to disturbances in the normal composition of the body, and the function of drugs was to bring about a readjustment of the proportions of the *tria prima*. Hitherto these drugs had been almost entirely of vegetable origin, but Paracelsus now advocated mainly inorganic

substances or substances of mineral origin. Many such substances, therefore, came to be prepared.

The teachings of Paracelsus the German Hermes and beloved Trismegistus, as his more enthusiastic disciples called him—exercised a great influence on the history of chemistry, for they not only weaned men's minds from the obsession of gold-making and from "the deceitful and mischievous art of alchemy," as Leonardo da Vinci called it, but they also led to the preparation and study of many new materials. Iatrochemistry, therefore, acted as the necessary link between the alchemy of the fifteenth and the beginnings of an exact science of chemistry in the seventeenth century, of which the herald was the Hon. ROBERT BOYLE.

### CHAPTER III

#### THE DAWN OF CHEMISTRY

ROBERT BOYLE, the youngest son and fourteenth child of the First Earl of Cork, was born at Lismore, in Ireland, in 1627, the year after Francis Bacon died. After passing four years, between



ROBERT BOYLE.

From the Painting after F. Kerseboom.  
(*National Portrait Gallery, London*)

the age of eight and twelve, at Eton, Boyle spent six years in travel and study on the Continent—mainly at Geneva and Florence—before returning to his home, Stalbridge Manor, in Dorset. Despite the turmoil of Civil War, then raging in England, interest in natural knowledge was stirring, and there were

some who sought and found escape from the political and religious strife of the times in the quiet waters of scientific study and in the cultivation of experimental science, then called the "New Philosophy." About 1646 or 1647, Boyle, who was of a thoughtful and studious disposition and had shown some interest in physical science while at Florence, was introduced as a member of the *Philosophical College*, or, as it was humorously called, the *Invisible College*, because it had no fixed place of meeting. This College had been formed in London a year or two previously by a small number of men who were interested in experimental science, and in 1663 it developed into the Royal Society, one of a group of learned societies which reflected the newly-born scientific spirit of the time and which were established in the second half of the seventeenth century in England, France, Germany and Italy. The members of the College met from time to time for the discussion of philosophical and scientific questions, and adopted the experimental and inductive method of modern science as laid down by Francis Bacon, "being satisfied that there was no certain way of arriving at any competent knowledge unless they made a variety of experiments upon natural bodies."

Boyle's own experiments covered a fairly wide field. He improved the "pneumatic engine" or air pump which had been invented by Otto von Guericke, and studied therewith the "spring" or elastic power of the air. Through these experiments he was led to investigate the relationship between the volume and pressure of air, and established the generalisation known as Boyle's law. Boyle discovered, also, the dependence of the boiling point of a liquid on the pressure; he separated wood alcohol from the other products of the distillation of wood, prepared the important liquid, acetone, by heating the acetates of calcium and of lead, and introduced the mixture of ice and salt as a freezing mixture.

Important as were the experimental contributions to science made by Boyle, his chief claim to fame and honour depends on the views which he expressed in *The Sceptical Chymist*, published in 1661. In this book, which marks the beginning of a new era—the scientific era—in chemistry, Boyle breathed a new life and spirit into the science; and he gave to chemical study and practice not only a new motive and direction but a new method. No longer should the chief aim and motive of chemistry be to produce gold or to prepare drugs but, in complete freedom, to acquire a knowledge of the composition of different kinds of matter, "to find out nature, to see into what principles

things might be resolved, and of what they were compounded." Such knowledge could be gained only by the experimental method, not by deductive speculation. Boyle was the first to use the term *analysis*, the practice of which he encouraged for the purpose of ascertaining the composition of materials. He introduced a number of tests, still employed, for different elements, and he was the first to employ coloured plant products (*e.g.* litmus) for the detection of acids and alkalis.

In Boyle's time there was an absence of sound theory founded on experiment, and both the alchemists and the iatrochemists were obsessed by vague ideas about qualities or principles which, it was thought, could be added to or withdrawn from matter at will. Thereby a transmutation of matter or the curing of disease could be effected.

Casting off, however, the obscurity and mysticism of the alchemical writers who "by mystical terms and ambiguous phrases darken what they should clear up," Boyle pointed out that no real advance in chemical knowledge is possible until the vagueness and indefiniteness of the terms element, principle, quality, essence, etc., used by Aristotle and the mediæval alchemists, were swept away, and clearly defined notions put in their place. This Boyle does in *The Sceptical Chymist*, where, for the first time, the distinction is drawn between mixtures, compounds and elements, and the conception of an element is clearly formulated. "I mean by elements," wrote Boyle, "certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved." A more practical definition of an element, such as was given at a later date by Lavoisier, could not then be formulated.

The publication of *The Sceptical Chymist* may be said to mark the close of the alchemistic period and the birth of scientific chemistry. And yet, in spite of the force and clarity of Boyle's teaching, chemists could not easily free themselves from the spirit of mediæval thought. For a hundred years, the development of chemistry as an exact science was delayed owing to the domination of men's minds by the phlogiston theory of combustion with its underlying hypothesis of a vague "principle of combustibility." To a fuller consideration of this, we shall return in due course.

On December 31, 1691, Robert Boyle, the kindly, lovable, courteous and humble-minded nobleman and man of science, passed to his rest.

**The Aim and Scope of Chemistry.** Recognising the freedom and independence which Boyle claimed for chemistry, and accepting the new motive and direction which he gave to its study, one may briefly state the aim and scope of the science in the following terms :

Chemistry is a branch of science which deals with matter, or with the material universe which is revealed to us by our senses. It studies the different kinds of substances found in the world, whether in the living animal or vegetable organisms, or in the non-living mineral matter of the universe. Chemistry investigates the composition and specific properties of these substances, the methods of their preparation, the changes which they undergo, and their behaviour, not only in relation to what are called physical forces (heat, light, electricity, etc.), but also in relation to other substances.

In interpreting this definition, however, it is necessary always to bear in mind that chemistry, like other branches of science, has a spirit as well as a body. "It is not the particular facts of a science that constitute its vitality, but the generic facts or conceptions to which they have elevated the mind. Facts are the body of science, and the idea of those facts is its spirit."<sup>1</sup> Chemistry, therefore, must not be regarded merely as a collection of facts, or as a catalogue of preparations and properties. The chemist must seek not only to ascertain but also to interpret the phenomena of chemical transformation. He must not only study the *products* of chemical change, but he must also learn the laws according to which the *processes* of chemical change take place. Moreover, in his endeavour to interpret these laws, the chemist must concern himself also with the fundamental questions relating to the ultimate constitution and structure of matter, and to the forces which govern the changes and transformations which he observes in his laboratory, or which are wrought out in the larger laboratory of nature. Nor must it be forgotten that the frontier lines by which one has sought, arbitrarily and as a matter of convenience, to delimit the domains of physics and of chemistry, have to a great extent been swept away and obliterated by the tumultuous rush of new knowledge which has been a special feature of the twentieth century. There is, indeed, now, no more fruitful region of experimental and speculative activity than the common territory where the sciences of physics and chemistry overlap, and in the cultivation of which scientific workers—whether they call themselves, or are called by others, chemists or physicists—co-operate in the

<sup>1</sup> Samuel Brown, *The History of Science* (1846).



advancement of a knowledge of nature which is one and indivisible.

Since, in our everyday life as well as in carrying out industrial operations, we are concerned with matter and with changes and transformations of matter, it is clear that if we would understand these changes aright, and if we would carry out and control these changes so as to secure the greatest advantage from them, we must possess a knowledge of chemistry. On the science of chemistry, more than on any other branch of organised knowledge, depend the material well-being and comfort of man.

Chemistry, however, should be studied not merely for the sake of its practical applications and of its usefulness in improving old or in establishing new industries; chemistry, like other branches of science, possesses a cultural value, apart from its applications. Its study is not only a means of cultivating the mind and of training and strengthening the scientific habit of thought, but it also brings us into closer relations with and gives a fuller understanding of the physical universe in which we live. In the study of chemistry one must seek not only the knowledge by which material results may be achieved, but the understanding of its laws and theories by which alone intellectual satisfaction can be secured.

**Mixtures, Compounds, Elements.**—Even the most casual observation makes it evident to us that this universe is made up of a vast number of materials of very diverse kinds; and it is obvious that in order to obtain any effective scientific knowledge of the great array of materials, it is necessary to deal with them in the way we have learned that the scientist deals with the isolated data and facts of experience. *The materials must be ordered and classified.* For this purpose we can, and, in our everyday life, we do, make use of the impressions which the different materials make on our senses. Thus, by the sense of touch, we can distinguish a piece of coal from a piece of graphite, because of the greasy or unctuous feel of the latter; and our sense of sight enables us to distinguish different materials according to their colour—sulphur from bluestone (copper sulphate), red lead from malachite.

The impressions which a particular material makes on the senses constitute some of the *properties* of the material; and one might group the different materials in accordance with these sense impressions, as was, indeed, largely done in the early pre-scientific days. A classification, however, which depended entirely on direct sense impressions would not be sufficiently exact, and it is for this reason that in olden days materials which

we can now readily distinguish were thought to be the same. Malachite (copper carbonate), for example, was not clearly distinguished from emerald, and red lead (oxide of lead) was confused with cinnabar (sulphide of mercury). Other properties, therefore, besides those of direct sense impression, and more especially properties, *e.g.* density, which can be accurately measured or determined, must be taken into account.

On making a careful examination of the objects and materials around us, we find that they can be grouped into two large classes: *homogeneous bodies or materials* and *heterogeneous bodies or materials*. In the case of the former, the properties are the same in every portion of the material. Thus, if one examines a piece of sulphur, for example, one can detect no want of uniformity in the colour, such as would betray the presence of different kinds of matter. The mass is uniformly yellow throughout. Moreover, when a piece of sulphur is subjected to a more thorough examination, one learns, not only that, at the ordinary temperature, it is hard, but that it can readily be ground to a powder, and that when heated to a certain definite temperature, it melts or passes into the liquid state. When heated to a somewhat higher temperature in contact with the air, the sulphur takes fire and burns with a blue flame. At the same time, a gas with a choking smell is produced. When placed in water, the piece of sulphur sinks, but does not undergo any change. When brought in contact, however, with the colourless liquid called carbon disulphide, the sulphur disappears. It passes into solution or dissolves.

When one *tests*, or examines, the behaviour of other pieces of sulphur, it is found that all behave in exactly the same way. Each piece of sulphur, irrespective of its origin, size or shape, melts at the same definite temperature, has a certain density or specific gravity, dissolves in carbon disulphide but not in water, and burns in air with production of a choking gas. Clearly, then, these properties are characteristic of sulphur and enable one to place all pieces of sulphur into a group by themselves. Such characteristic properties are spoken of as *specific properties*—specific physical or specific chemical properties,<sup>1</sup> as the case may be—because they are the properties shown by a particular species or kind of matter.

Many other kinds of homogeneous matter are known,

<sup>1</sup> The density, colour, electrical properties, etc., which depend on the response of matter to certain physical agencies, are called physical properties. The behaviour of one kind of matter towards other kinds of matter, is a chemical property.

*e.g.* silver, lead, water, sugar, etc., each of these names connoting a group of properties which are definite for each particle of a particular kind of homogeneous matter.

*We reach, therefore, the very important conclusion that different homogeneous materials can be arranged in groups, so that the members of each group are characterised by certain specific properties.*

In the case of heterogeneous matter, *e.g.* granite, the properties are, of course, not uniform throughout the whole mass. Different portions have different properties, each of these portions, however, being in itself homogeneous or uniform in properties throughout. Heterogeneous matter is, therefore, a *mixture* of two or more homogeneous portions of matter, these homogeneous portions being known as the constituents or ingredients of the mixture.

In these heterogeneous mixtures, it will be understood, the constituents retain their specific properties, so that it is possible, by appropriate means, to separate them from one another. If one mixes together, for example, a fine powder of iron with finely powdered sulphur, a grayish-green coloured material is obtained. Since, however, the iron and the sulphur retain their specific properties, their separation can be effected by means of a magnet. The iron is attracted by the magnet, the sulphur is not. Or, one may separate the iron and sulphur, also, by shaking the mixture with carbon disulphide. The sulphur dissolves in the carbon disulphide, the iron does not. The solution is then separated from the iron by filtration through filter paper (Fig. 2), and the sulphur recovered by evaporating off the carbon disulphide.

Filtration is a process which can be applied generally for the separation of solid particles from a liquid, the filter consisting of some porous material—unsized paper, cloth, biscuit-ware, etc.—the pores of which are too small to allow the solid particles to pass through.

In arranging the diverse materials into groups of homogeneous matter, characterised by specific properties, the chemist is only at the beginning of his task; for, on investigating the groups of homogeneous matter more thoroughly, differences of behaviour

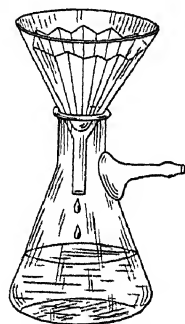


FIG. 2.—Filtration.

The liquid to be filtered is poured into a "cone" of filter paper. The liquid passes through the paper and flows down the stem of the funnel, but the solid is retained.

are found which make a further subdivision necessary. To understand this, it will be well to carry out a few simple experiments.

It is a familiar fact that when water is heated to a certain temperature, it boils and passes into vapour; and if this vapour is cooled down, it condenses to liquid water. This process, which is known as *distillation* and which was one of the earliest operations to be carried out by Egyptian and Arabian craftsmen for the purpose of preparing drugs and ethereal oils from plants, can be very conveniently carried out in the apparatus shown in Fig. 3. Water is boiled in the flask, and the vapour which passes out through the tube in the neck of the flask is led into the central tube of the *condenser*, where it is cooled down by

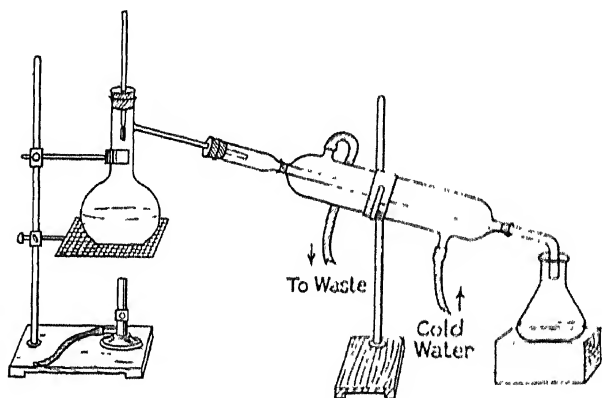


FIG. 3. Distillation.

a surrounding current of cold water. The condensed vapour flows into the *receiver*. A thermometer, inserted through a cork in the neck of the flask, shows the temperature of the vapour passing into the condenser. This temperature remains constant during the process of distillation. On examination, the *distillate* is found to have exactly the same properties, *e.g.* the same density, as the original water. By subjecting water to the process of distillation, no change is effected in the properties of the liquid.

Many other liquids, the names of which are familiar to all, such as spirits of wine, ether, chloroform, etc., behave in the same way. Their properties are unaltered by distillation.

All homogeneous liquids, however, do not behave in this way. As early, at least, as the tenth century, and probably much earlier, it was known to sailors that a water fit for drinking

could be obtained by the distillation of sea-water; <sup>1</sup> and it was also known in the tenth century that when wine is distilled, an "inflammable water" is obtained which is different from the wine and which "burns away without consuming the material on which it is poured." This is, indeed, the earliest reference to the preparation of "spirits of wine," or alcohol.

When sea-water is distilled, water vapour only is given off, and this is condensed to liquid water, identical with that which was obtained by the distillation of water; and there remains, at last, in the flask or *still*, after all the water has passed away, a white solid, which is really a heterogeneous mixture of common salt and various other substances. By the process of distillation, therefore, the homogeneous liquid, sea-water, has been separated into a liquid and a solid material. If the liquid distillate and solid residue are mixed together, a liquid is obtained which is identical with the original sea-water.

Again, when spirits of wine and water are brought together, they mix thoroughly and form a homogeneous liquid. When this liquid is distilled, quite a different behaviour is shown from that which is shown by water or by alcohol alone or by sea-water, owing to the fact that both constituents of the mixture are volatile. When water or alcohol or sea-water is distilled, the temperature of the condensing vapour remains unchanged during the whole process; but when the mixture of water and alcohol is distilled, the temperature slowly rises as the process continues. This points to a progressive change in the nature of the condensing vapour. Moreover, if the liquid which distils over is collected in a number of portions or *fractions*, the different fractions are found to have different properties. The first fractions, for example, have a lower density than the later fractions, and they give off a more readily inflammable vapour, as can be shown by placing the liquid in a shallow dish and passing a lighted taper over its surface. In fact, the liquid which first comes over is nearly pure alcohol, while the liquid which comes over at the end is nearly pure water. If all the fractions of the distillate are mixed together, a homogeneous liquid, identical with the original liquid, is obtained.

From the experiments which have just been described, it will be clear that a homogeneous body can, in some cases, be separated into different kinds of matter by means of some simple process based on a difference of physical properties (in the above cases, difference of volatility) of the constituent materials;

<sup>1</sup> According to Alexander of Aphrodisias (third century), the distillation of sea-water was already known in his time (A. von Humboldt, *Cosmos*).

and the original material can be reproduced simply by bringing the constituents together. In other cases, as in the case of water or of alcohol, no such separation is possible. Every portion or fraction of the distillate and of the residue in the still is identical.

Two kinds of homogeneous matter, therefore, can be distinguished: 1. Homogeneous matter which can be separated into different constituents by some simple process which is based on a difference of physical properties of the constituents. During the process of separation, the properties of the original matter change continuously. 2. Homogeneous matter which cannot be so separated. To the former kind of homogeneous matter there is given the name of homogeneous mixture or *solution*; to the latter, the name of *substance* or *pure substance*, a substance being characterised by a definite group of specific properties.

The classification of the different kinds of matter which experimental investigation enables one to make, is not yet complete. Pure substances, as Boyle pointed out, can be divided into two classes. In the one class are those which, like sulphur or iron, have, so far, resisted all attempts to decompose them, or to break them down into substances simpler than themselves. These substances, according to Boyle, are the true *elements*, and this definition of an element, due essentially to Lavoisier, is still retained. The definition, it should be noted, does not assert the impossibility of decomposition, but insists merely on the fact that the possibility, if it exist, has not so far been realised.<sup>1</sup> Although this definition may still serve for most purposes, modern knowledge regarding the constitution of matter, to which reference will be made in a later chapter, shows the need of a new definition.

In the second class of pure substances are placed those which, by one means or another, can be resolved into simpler substances. These more complex substances are called *compounds*. Thus, if one heats in a tube, called a *test-tube*, the red-coloured substance known as red precipitate or oxide of mercury, globules of a shining liquid, shown by appropriate tests to be mercury, are deposited on the walls of the tube. No other new substance is observed, but if a glowing splint of wood is inserted into the tube, it bursts into flame, showing that there is some gas in the tube which is different from ordinary air. The red solid, there-

<sup>1</sup> "We cannot be certain," wrote Lavoisier in 1789, "that what we think to-day to be simple is indeed simple; all we may say is, that such or such a substance is the actual term at which chemical analysis has arrived, and that with our present knowledge we are unable to subdivide farther."

fore, has been broken up by heat into a shining liquid (mercury) and an invisible gas, which we shall get to know later as oxygen. On allowing the tube to cool down, it is found that the remaining oxide of mercury has exactly the same properties as at the beginning of the experiment, although, of course, there is now less of it. Since no other substances besides mercury and oxygen are obtained from the red oxide of mercury, it is concluded that this substance is a compound of mercury and oxygen.

Based on the clear-sighted views of Boyle and as the result of numerous experimental investigations, chemists have reached the following classification of the different kinds of matter which we recognise as making up our external universe :

I. Heterogeneous Matter or Heterogeneous Mixtures.

II. Homogeneous Matter.

(1) Homogeneous Mixtures or Solutions.

(2) (Pure) Substances.

(a) Elements.

(b) Compounds.

Since both homogeneous mixtures and compounds can be broken up or separated into two or more different substances, the question arises : How can one distinguish between them ? Various criteria can be applied.

1. A homogeneous mixture can be separated, more or less completely, into its constituents by taking advantage of their different physical properties, *e.g.* density, solubility, volatility, magnetic properties, etc. In the case of a compound, this cannot be done.

Thus, a mixture of hydrogen and oxygen can be separated to a greater or less extent by shaking with water, because oxygen is more soluble than hydrogen. If, however, the mixture of hydrogen and oxygen is heated above a certain temperature, a flash of light is seen, heat is evolved, and, in place of the gaseous mixture, we obtain liquid water. The properties of hydrogen and oxygen have entirely disappeared and a new substance with its own specific properties has made its appearance. The hydrogen and oxygen have combined to form the *compound* water.

Further, a solution of salt in water or of alcohol in water can, as we have already learned, be separated into its constituents by distillation owing to a difference in the volatility of the constituents.

2. The composition of a mixture may vary *continuously*, but a compound *always has a definite and constant composition*. Thus, varying amounts of salt can be dissolved in water, and as the amount of salt is varied the composition and the properties

of the solution, *e.g.* the density, vary continuously. The properties of a solution, therefore, depend on the composition. In the case of a compound, the composition is fixed and the specific properties are constant under given external conditions, say of temperature and pressure.

Although the application of the above criteria will enable one to distinguish, in most cases, between a homogeneous mixture and a compound, it must be borne in mind that frequently no single test will be adequate.

### THE CHEMICAL ELEMENTS

Although it was Boyle who first laid the foundation on which a true science of chemistry might be built, a hundred and twenty years had to elapse before the teachings of the "Sceptical Chymist" were generally recognised and accepted by chemists; and it was only after Lavoisier had given the true explanation of combustion and had, in his *Traité élémentaire de chimie* (1789), reiterated more clearly Boyle's teaching that the object of chemistry is "to decompose the different natural bodies and . . . to examine separately the different substances which enter into their combination," that the work of analysing, ordering and classifying the different kinds of matter became one of the main preoccupations of chemists. Ever since that time this work has been going on, and it now appears, so far as our present day knowledge warrants a judgment, almost to have reached finality.

The new life inspired into the science by Lavoisier led to an increasingly active investigation of different materials, and the number of substances recognised as elements rapidly grew as the methods and technique of analysis were improved and as new and more powerful agents of decomposition were discovered. Thus, the decomposing action of the electric current, the application of which was made possible by the invention of the voltaic cell, led, in the hands of Humphry Davy, to the isolation, in 1807, of potassium, sodium, calcium, strontium and barium; and the introduction of spectroscopic analysis, in 1860, and of the modern methods of X-ray spectroscopy, have led to the discovery of a number of rare elements which otherwise might have remained unknown. In 1800, the number of known elements was 28; in 1830, it was 54; in 1860, it was 56; in 1900, it was 73; and at the present time it is 90. This number, however, does not include all the so-called "radio elements" which are continuously undergoing a process of spontaneous disintegration and which lead a more or less transitory life. A list of the elements is given in the following table.



## LIST OF THE ELEMENTS (1929)

Atomic number	Symbol	Atomic weight	Atomic number	Symbol	Atomic weight
1. Hydrogen . . .	H	1.008	47. Silver . . .	Ag	107.88
2. Helium . . .	He	4.00	48. Cadmium . . .	Cd	112.40
3. Lithium . . .	Li	6.94	49. Indium . . .	In	114.8
4. Beryllium . . .	Be	9.02	50. Tin . . .	Sn	118.7
5. Boron . . .	B	10.83	51. Antimony . . .	Sb	121.76
6. Carbon . . .	C	12.004	52. Tellurium . . .	Te	127.5
7. Nitrogen . . .	N	14.008	53. Iodine . . .	I	126.93
8. Oxygen . . .	O	16.00	54. Xenon . . .	Xe	130.2
9. Fluorine . . .	F	19.00	55. Caesium . . .	Cs	132.81
10. Neon . . .	Ne	20.18	56. Barium . . .	Ba	137.36
11. Sodium . . .	Na	23.00	57. Lanthanum . . .	La	138.9
12. Magnesium . . .	Mg	24.30	58. Cerium . . .	Ce	140.2
13. Aluminium . . .	Al	26.97	59. Praseodymium . . .	Pr	140.9
14. Silicon . . .	Si	28.1	60. Neodymium . . .	Nd	144.3
15. Phosphorus . . .	P	30.98	61. ILLINIUM . . .	Il	—
16. Sulphur . . .	S	32.06	62. Samarium . . .	Sa	150.4
17. Chlorine . . .	Cl	35.46	63. Europium . . .	Eu	152.0
18. Argon . . .	A	39.94	64. Gadolinium . . .	Gd	157.0
19. Potassium . . .	K	39.10	65. Terbium . . .	Tb	159.2
20. Calcium . . .	Ca	40.09	66. Dysprosium . . .	Dy	162.5
21. Scandium . . .	Sc	45.1	67. Holmium . . .	Ho	163.5
22. Titanium . . .	Ti	47.90	68. Erbium . . .	Er	167.6
23. Vanadium . . .	V	50.95	69. Thulium . . .	Tm	169.4
24. Chromium . . .	Cr	52.04	70. Ytterbium . . .	Yb	173.0
25. Manganese . . .	Mn	54.95	71. Lutecium . . .	Lu	175.0
26. Iron . . .	Fe	55.84	72. Hafnium . . .	Hf	178.6
27. Cobalt . . .	Co	58.95	73. Tantalum . . .	Ta	181.3
28. Nickel . . .	Ni	58.69	74. Tungsten . . .	W	184.1
29. Copper . . .	Cu	63.55	75. Rhenium . . .	Re	—
30. Zinc . . .	Zn	65.38	76. Osmium . . .	Os	191.0
31. Gallium . . .	Ga	69.72	77. Iridium . . .	Ir	193.0
32. Germanium . . .	Ge	72.60	78. Platinum . . .	Pt	195.2
33. Arsenic . . .	As	74.93	79. Gold . . .	Au	197.2
34. Selenium . . .	Se	79.2	80. Mercury . . .	Hg	200.6
35. Bromine . . .	Br	79.92	81. Thallium . . .	Tl	204.0
36. Krypton . . .	Kr	82.9	82. Lead . . .	Pb	207.2
37. Rubidium . . .	Rb	85.4	83. Bismuth . . .	Bi	209.0
38. Strontium . . .	Sr	87.63	84. Polonium . . .	Po	—
39. Yttrium . . .	Yt	88.93	85. — . . .	—	—
40. Zirconium . . .	Zr	91.2	86. Niton <sup>1</sup> . . .	Nt	222.0
41. Niobium . . .	Nb	93.3	87. — . . .	—	—
42. Molybdenum . . .	Mo	96.0	88. Radium . . .	Ra	225.95
43. Masurium . . .	Ma	—	89. Actinium . . .	Ac	—
44. Ruthenium . . .	Ru	101.7	90. Thorium . . .	Th	232.15
45. Rhodium . . .	Rh	102.9	91. Protoactinium . . .	Pa	—
46. Palladium . . .	Pd	106.7	92. Uranium . . .	U	238.2

As the result of a very large amount of labour and experimental investigation, chemists have not succeeded in reducing the number of the elements to less than 90. From these elements, all the different substances, approaching half a million in number, which are found in nature or which can be prepared

<sup>1</sup> Also called Radon (Rn).

in the laboratory, are built up; and they represent the limit of simplification so far reached by the chemist in his attempt to classify the materials of the universe. The much greater simplification which has been achieved in recent years by the physicist, will be discussed at a later point.

Of the elements mentioned in the table, many have been obtained only in very small amounts; and analysis has shown that 99 per cent. of terrestrial matter is made up of about twelve elements, some of which occur in the elementary state, but most of them in the form of compounds.

CHEMICAL COMPOSITION OF TERRESTRIAL MATTER  
(EARTH, AIR AND SEA)

	Per cent.		Per cent.
Oxygen . . . . .	50.02	Potassium . . . . .	2.28
Silicon . . . . .	25.80	Magnesium . . . . .	2.08
Aluminium . . . . .	7.30	Hydrogen . . . . .	0.95
Iron . . . . .	4.18	Titanium . . . . .	0.43
Calcium . . . . .	3.22	Chlorine . . . . .	0.20
Sodium. . . . .	2.36	Carbon . . . . .	0.18
			99.00

From the numbers in this table we learn that the two elements, oxygen and silicon, in the free or in the combined state, constitute together three-quarters of the whole of terrestrial matter, by weight, so far as this is accessible to direct investigation.

If one considers the composition merely of the earth's crust accessible to investigation, the average values do not greatly differ from those given above.

AVERAGE COMPOSITION OF THE EARTH'S CRUST

	Per cent.		Per cent.
Oxygen . . . . .	46.43	Potassium . . . . .	2.00
Silicon . . . . .	27.77	Magnesium . . . . .	2.00
Aluminium . . . . .	8.14	Titanium . . . . .	0.629
Iron . . . . .	5.12	Phosphorus . . . . .	0.130
Calcium . . . . .	3.63	Hydrogen . . . . .	0.127
Sodium. . . . .	2.85	Manganese . . . . .	0.096
			99.612

The numbers given in the above tables, it must be remembered, in so far as they refer to the solid earth, represent the composition only of the crust of the earth; a comparatively thin skin of about ten miles in thickness. Since this is only a small fraction (one per cent. or so) of the total globe, it is clear that it would

be very unwise to regard the numbers given in the above table as representing the composition of the earth as a whole. There is, indeed, much evidence to show that the composition of the interior of the earth is very different from that of the thin crust, which is all that has so far been subjected to a chemical analysis. Thus it is found that while the average density of the crust is 2.79, the average density of the earth as a whole is 5.52; and it is therefore clear that towards the centre of the earth, the heavier elements must be present in greater abundance than in the crust. From the investigation of the compressibility of rocks and from a study of seismological, magnetic and other data, the conclusion has been drawn that beneath the crust of the earth, which is essentially granitic or basaltic in composition, there occur zones diminishingly rich in silicates and increasingly rich in iron, and that there is, lastly, a core consisting essentially of iron and nickel. On the basis of these studies, moreover, H. S. WASHINGTON, of the Geo-physical Laboratory, Washington, D.C., has made the following calculation of the total composition of the earth :

TOTAL COMPOSITION OF THE EARTH

	Per cent		Per cent.
Iron . . . . .	39.76	Sodium . . . . .	0.39
Oxygen . . . . .	27.71	Cobalt . . . . .	0.23
Silicon . . . . .	14.53	Chromium . . . . .	0.20
Magnesium . . . . .	8.69	Potassium . . . . .	0.14
Nickel . . . . .	3.16	Phosphorus . . . . .	0.11
Calcium . . . . .	2.52	Manganese . . . . .	0.07
Aluminium . . . . .	1.79	Carbon . . . . .	0.04
Sulphur . . . . .	0.64	Titanium . . . . .	0.02

It is very noteworthy that the spectroscopic analysis of the sun's atmosphere has given results which show that there is a remarkable correspondence between its composition and that of the earth as a whole; a striking testimony to the kinship of the earth with the sun, from which, also, conclusions may be drawn regarding the history and evolution of the earth. Spectroscopic analysis, moreover, has not revealed the presence in the sun or stars of any element not known on the earth, and we may therefore assume an essential similarity between the composition of the earth, the sun and the stars.

#### Classification and General Characteristics of the Elements.

—In studying the properties of the elements and of the compounds which they form, it is usual to classify the elements into the two groups, the *metals* and the *non-metals*. Although it is not possible, at this stage, to discuss fully the distinctive properties of these two classes of elements, it may be said that

under the ordinary conditions of temperature and pressure, the metals, *e.g.* gold, silver, copper, iron, etc., are solids, the only exception being mercury, which is a liquid. Metals, also, are characterised by being relatively good conductors of heat and electricity, by showing, when in a coherent state, metallic lustre, and by being relatively malleable and ductile.

Of the non-metallic elements, it is found that, under ordinary conditions, some are solid (*e.g.* sulphur, phosphorus, carbon), one is liquid (bromine), and a number are gases (*e.g.* oxygen, nitrogen, hydrogen).

## CHAPTER IV

### THE FUNDAMENTAL LAWS OF CHEMISTRY

THE century and a half which followed the publication of *The Sceptical Chymist* was one of great expansion and of notable achievement in the study and advancement of chemistry. Inspired, doubtless, by the teaching of Boyle and with minds freed from the vain dreams of the alchemists and the restrictive outlook of Paracelsian philosophy, men devoted themselves, in ever-increasing numbers, to the study of chemistry with the sole motive of discovering the truths of nature and of extending the bounds of knowledge concerning the material universe. Thus, the eighteenth century saw the birth and rapid expansion of "pneumatic chemistry," or the chemistry of gases, and many new gases were prepared and their properties investigated, more especially by Scheele in Sweden and by Priestléy in England. Unfortunately, however, chemistry was dominated, during a large part of the century, by an erroneous interpretation of the phenomena of combustion and of other chemical processes; and although, doubtless, experimental research was stimulated and very great additions were made to the store of experimentally determined knowledge, the development of chemistry, on its theoretical side, was retarded. Boyle, it is true, had raised chemistry to the rank of a science, but it was not till towards the end of the eighteenth and the beginning of the nineteenth century that it became an exact science. Until then, the isolated facts of chemistry were not linked together by quantitative laws, nor were its laws interpreted by exact and definite theory capable of quantitative expression.

During the later decades of the eighteenth century the methods and technique of analysis—both qualitative and quantitative—were greatly extended and improved, more especially by the Swedish chemist and mineralogist, TORBERN OLOF BERGMAN (1735–1784); and the quantitative study of chemical processes and transformations, recognition of the importance of which is one of the most characteristic features of the century, was greatly developed. Although Black (1728–1799),

Cavendish (1731–1810) and Bergman had all made use of the balance in the study of chemical processes, it is to the brilliant French chemist, LAVOISIER, that is due the credit of inaugurating a new epoch—the quantitative epoch in chemistry.

ANTOINE LAURENT LAVOISIER, a native of Paris, was born in 1743 and showed at an early age great interest in and aptitude for scientific investigation ; and although, as a young man, he



ANTOINE LAURENT LAVOISIER.

pursued the study of law and qualified as an advocate, it was to the cultivation and advancement of science, and more especially of chemistry, that his life was devoted. By far the most brilliant chemist of the eighteenth century, Lavoisier, although not always scrupulous in acknowledging his indebtedness to others, made many contributions of the greatest importance to chemistry, both pure and applied. He showed, for example, that organic substances such as alcohol, oil and wax, are compounds containing the element carbon, and that the diamond is pure carbon ; as a member of various Commissions he wrote reports on agriculture and mining, on saltpetre production and on other sub-

jects, and he improved the manufacture of French gunpowder to such a degree that it became the best in Europe. As a consequence of this, it may perhaps be justly claimed that the American colonists, who were supplied with this powder during the War of Independence, owed to the chemist Lavoisier a debt no less real and no less great than that which they owed to his compatriot, the soldier Lafayette.

It is, however, with the overthrow of the phlogiston theory of combustion, the story of which will be told later, that the name of Lavoisier is most distinctively and most honourably connected; and in this great work, the completion of which marks the beginning of a new era in chemistry, Lavoisier's success was due mainly to his recognition of the supreme importance of studying chemical processes quantitatively, and to his adoption of the balance as an essential aid in the interpretation of the course of chemical action. To this, also, we owe the enunciation and verification by Lavoisier, in 1785, of the law of the indestructibility of matter or the conservation of mass.

In 1768, Lavoisier became a member of the *Ferme Générale*, a financial syndicate which, in return for an annual contribution to the royal treasury, had the right, under royal charter, of controlling the leases of royal domains and of collecting indirect taxes, customs and revenues. His membership of the syndicate brought him wealth which he freely spent in the advancement of science, but it cost him, at the last, his life. Denounced by Marat, Lavoisier was brought to trial, along with other members of the *Ferme Générale*, on the trumped-up and trivial charge of acting contrary to the common weal and of adulterating the tobacco of the people, and was condemned to death. One voice, only, was raised in protest, that of the chemist Loysel, who pleaded in his favour the great scientific services which Lavoisier had rendered to the State; but the only reply he received was that of Coffinhal, the President of the tribunal, *La République n'a pas besoin de savants*. The sentence of death was carried out on May 8, 1794.

The victim of a political and social revolution, Lavoisier was the author of a chemical revolution. By replacing the phlogiston theory by one which, as Black wrote, "is simpler, easier and better sustained by facts," Lavoisier gave to the study of chemistry a new life and a wider outlook, and, in association with Guyton de Morveau, Fourcroy and Berthollet, he gave it also a new language in which to express itself. In the chemical revolution inaugurated and inspired by Lavoisier, modern scientific chemistry, based on the law of the conservation of

mass and on a quantitative study of chemical processes, was born.

**Law of the Conservation of Mass.** Lavoisier was not the first to hold or to state the view that matter is indestructible, for this was a dogma of ancient Greek philosophy; and Democritus, more than 2000 years ago, taught that it is not possible for anything to arise out of nothing or to pass into nothingness. Many others held the same view and restated the law, which they regarded as axiomatic. During the Middle Ages, however, the opposite view was also held, and, indeed, seemed a most natural one at a time when the material nature of gases was not fully realised. The burning of a wood log or of a candle was surely evidence enough that matter is destroyed in the process of combustion. The assumption could be subjected to the test of experiment, however, only after Newton had made it clear in his *Principia* (1686), that "the weights of bodies towards any the same planet at equal distances from the centre of the planet, are proportional to the quantities of matter which they severally contain," and when it was recognised, that as regards matter, "weight and reality are correspondent" (Boerhaave, 1727). The truth or falsity of the view could thereafter be put to the test of the balance.

The law of the indestructibility of matter, or, as it is more properly called, the law of conservation of mass, was arrived at by Lavoisier deductively rather than inductively. Lavoisier assumed throughout all his work that matter is neither created nor destroyed in chemical change, and since the conclusion to be drawn from this, namely, that the total weight or mass before and after a chemical reaction must remain unaltered, was verified by his experiments, he enunciated the law in the following words: "Nothing is created, either in the operations of art or in those of nature, and it may be considered as a general principle that in every operation there exists an equal quantity of matter before and after the operation; that the quality and the quantity of the constituents is the same, and that what happens is only changes, modifications."

In one of the experiments which Lavoisier carried out, tin was heated in a closed flask filled with air until the metal was converted into its calx (oxide). The flask with its contents was weighed before and after the heating, and it was found that there was a slight loss of weight amounting to from 0.27 to 1.0 grain. This difference in weight was attributed by Lavoisier to experimental error.

The determinations of Lavoisier were, according to present



day standards, rather coarse and inaccurate, and changes of weight of less than about 0.2 per cent. could not be detected. Experiments of a very high degree of accuracy, however, were carried out, in 1908, by H. LANDOLT (1831–1910), Professor of Physical Chemistry in the University of Berlin, and, in 1912, by J. J. MANLEY, of Magdalen College, Oxford. The reacting substances, in solution, were introduced through the side-tubes,  $t_1$  and  $t_2$ , into the two limbs of the reaction vessel (Fig. 4), the side-tubes being then hermetically sealed. After the vessel and its contents had been carefully weighed, the two solutions were mixed; and after the reaction had taken place, the vessel was again weighed. As a result of these determinations, it was shown that if a change of weight occurs in a chemical reaction, that change does not exceed one part in one hundred million. With this degree of accuracy, at least, the law of conservation of mass is valid. Restating the law, therefore, with this limitation in mind, we may say: *In no case is there any change in the total mass of the substances taking part in a chemical reaction; the total mass of the substances under-*

*going change is equal to the total mass of the substances produced.* On this law is based the whole edifice of quantitative chemistry.

#### Dalton's Atomic Theory and the Laws of Chemistry.—

During the latter part of the eighteenth century, as has been pointed out, increasing attention was given to the quantitative study of chemical processes, and a considerable number of facts relating to the quantitative relations of chemical combination were accumulated. At the beginning of the nineteenth century, therefore, the time was fully ripe for the enunciation of a theory, based on definite conceptions regarding the constitution of matter, by which the experimental results might be co-ordinated and interpreted.

The general hypothesis of the atomic constitution of matter, we have seen, was put forward by the Epicurean philosophers of ancient Greece, and was expounded by the Roman poet, Lucretius. Owing to the long-continued intellectual dominance of the philosophy of Aristotle, however, the atomistic hypothesis fell into an oblivion from which it was rescued in the sixteenth century by the physicist Gassendi. In the following century,

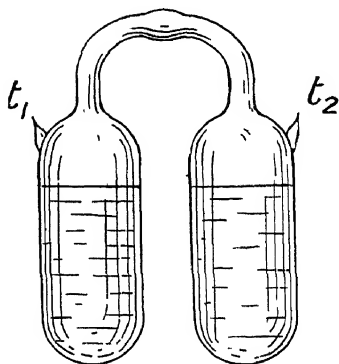


FIG. 4.—Manley's reaction vessel.

the hypothesis received the powerful support of Newton whose views regarding the nature of the atoms were expressed in the words: "It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which he formed them; and that those primitive particles, being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in the first creation."

The general hypothesis of the atomic constitution of matter, however, as expounded by Lucretius or as accepted by Newton, remained little more than an interesting speculation. It had no real value in science and had no influence on the progress of chemistry, for it was not possible either to test deductions from the hypothesis by means of experiment or to use it in the interpretation of the laws of chemistry. Not until the fundamental hypothesis had been developed in such a way that deductions from it could be put to the test of experiment and that the observed phenomena and the laws of chemical combination could be quantitatively explained or co-ordinated, could the hypothesis of the atomic constitution of matter become of any real value in science. This development of the hypothesis we owe to the Manchester schoolmaster, John Dalton.

JOHN DALTON, the son of a hand loom weaver, was born at Eaglesfield, in Cumberland, in 1766. A boy evidently of unusual ability, he opened a school in his native village and began to teach at the age of twelve. In 1793 he obtained a post as teacher of mathematics, natural philosophy and chemistry at the Manchester New College, a school at which, before its removal from Warrington to Manchester, Priestley also had been a teacher. His spare time was spent in the laboratory and in meditation on the properties of matter, and in order that he might have greater leisure for the pursuit of his scientific work, he resigned his teaching post in 1799 and became a private tutor. The atomic theory, on which his fame mainly rests, was made public in 1807. A man of quiet, retiring and modest character, Dalton found his greatest satisfaction in the pursuit of scientific truth. With his achievements and name recognised and honoured both at home and abroad, Dalton died in Manchester in 1844.

Accepting the thesis of Newton that gases are composed of small and mutually repellent particles or atoms of matter, Dalton, it is believed, built up his theory not inductively from a consideration of and grouping together of related phenomena, but deductively on the basis of the following postulates :

1. The atoms of matter, which are indivisible, eternal and indestructible, differ in their nature.



JOHN DALTON.

Reproduced from the portrait by Faulkener  
by permission of the Royal Society.

2. In the case of any particular element the atoms are all alike in their properties and have, more especially, the same mass ; but they differ in their properties from the atoms of other elements.
3. Compounds are formed by the combination of atoms of different kinds.

What deductions, then, can be drawn from these postulates ?

Since the atoms are assumed to be eternal and indestructible, it follows that matter, which is made up of atoms, is also indestructible ; and since the amount of matter is determined by weight or mass, we reach the conclusion that there can be no change of weight or mass in any chemical transformation. This

is the *law of conservation of mass* which, as we have learned, has been verified experimentally with an accuracy of one part in one hundred million.

**Law of Constant Composition.**— From the postulates of Dalton it may further be deduced that, since compounds are formed by the combination of atoms, the nature and properties of the compound must depend on the number and kind of the atoms present. In other words, the composition of a compound must be definite and constant. This is the *law of constant composition*.

During the closing years of the eighteenth and opening years of the nineteenth century, quite a considerable and interesting controversy arose round the question whether the composition of a compound is or is not constant and definite. CLAUDE LOUIS BERTHOLLET (1748–1822), one of the most eminent and honoured chemists of his day and a companion of Napoleon on his expedition to Egypt in 1799,<sup>1</sup> drew, from his experiments, the erroneous conclusion that the composition of a compound may vary; but this conclusion was hotly contested by another French chemist, JOSEPH LOUIS PROUST (1755–1826), at that time Professor of Chemistry at Madrid, who, by a large number of accurate analyses, showed that the composition of a compound is constant and definite, no matter how or where prepared. “The cinnabar of Japan has the same composition as the cinnabar of Almaden; . . . in all the known parts of the world you will not find two muriates of soda [common salt] . . . differing from each other.”

Even as late as 1860, however, the suggestion continued to be made that the composition of a compound might vary within very small limits, but the celebrated Belgian chemist, JEAN SERVAIS STAS (1813–1891), prepared silver chloride in four different ways and showed that if differences in composition exist, these must be less than the error of experiment, or less than 0.004 per cent. Many other analyses by Stas and by others have served to verify, with all the accuracy at present attainable, the law of definite and constant proportions which was first arrived at deductively and with which the assumptions of the atomic theory are in harmony.<sup>2</sup>

**Law of Multiple Proportions.** Although it is true that, as Jean Rey wrote in 1630, “nature has set limits which she does not overstep,” this must not be interpreted as meaning that nature has set only one limit to the proportions in which two

<sup>1</sup> Of Berthollet, Sir Humphry Davy wrote: “Berthollet was a most amiable man; when the friend of Napoleon even, always good, conciliatory and modest, frank and candid. He had no airs and many graces.”

<sup>2</sup> As will be discussed later, this statement now requires some qualification, in view of the existence of isotopes.

elements may combine to form a compound. It was quite well known to Proust and others that elements may unite with one another in more than one proportion, to form two or more compounds, each of which has a definite composition. Thus, the metal tin can combine with the element oxygen so as to form two compounds. In one of these, there is 11.9 per cent. of oxygen, and in the other, 21.2 per cent. No compound of intermediate composition is known. Other cases of a similar character were also found, but Dalton was the first to discover a simple definite relation between the different proportions in which the elements combine; and to the making of this discovery, he was guided by his atomic theory. Since the fundamental assumption of the atomic theory is that atoms are indivisible, it follows that combination can take place only between whole numbers of atoms. That is to say, when two elements A and B combine to form compounds containing different proportions of A and B, the compounds so formed must be represented by  $A+B$ ,  $A+2B$ ,  $2A+B$ ,  $2A+3B$ , etc. In other words, *when one substance combines with another substance in more than one proportion, these different proportions stand to one another in the ratio of integral, and generally small, numbers.* This is the *law of multiple proportions*—the second fundamental law of chemical combination.

Dalton was led to the discovery of this law from a consideration, in the first place, of the proportions in which carbon and hydrogen combine to form the compounds methane or marsh gas and ethylene. Expressing the composition of these two gases in terms of our present knowledge, it is found that in the case of marsh gas 12 parts by weight of carbon are combined with 4 parts by weight of hydrogen; whereas, in the case of ethylene, 12 parts of carbon are combined with 2 parts of hydrogen. The amount of hydrogen combined with a given amount of carbon is twice as great in the case of marsh gas as it is in the case of ethylene.

A still more striking illustration of the law of multiple proportions is found in the series of compounds which are formed by the combination of nitrogen and oxygen, to which reference will be made later.

According to the theory of Dalton, as we have learned, the atoms of the elements have a definite mass, and it was the introduction of this quantitative factor into the hypothesis of the atomic constitution of matter which made the atomic theory the foundation stone of physical science during the nineteenth century. Although it is possible, on the basis of the experi-

mental investigations of the present century, to calculate the absolute masses of atoms, it is not with these absolute masses but with the *relative* masses of the atoms that chemistry is concerned. These relative masses or relative weights of the atoms can be determined by methods which will be discussed at a later point, and such determinations constitute one of the greatest achievements of science, following in the train of Dalton's atomic theory. These relative weights are what are called the *atomic weights* of the elements, and their values are given in the table on p. 45. Since these atomic weights are only relative weights, we can select any element we please as standard and put its atomic weight equal to unity or to any other number. For long, atomic weights were referred to the atomic weight of hydrogen which was put equal to unity, but, by international agreement, oxygen is now taken as the reference element and its atomic weight put equal to 16.00. On this scale, the atomic weight of hydrogen is 1.008.

At first, Dalton made no distinction between the smallest particle of an element and the smallest particle of a compound. Both were called atoms. It is clear, however, that this must cause difficulty, because although the atom of an element may be regarded as indivisible, the atom of a compound must be capable of being split up into smaller particles, namely, the atoms of the component elements. A new name was therefore introduced by the Italian physicist, AMEDEO AVOGADRO (1776-1856), Professor of Physics at Turin, who called the smallest particle of a compound a *molecule*. We have, then, the definition that an atom is the smallest particle of an element which can enter into the composition of a molecule, or which can take part in chemical exchange. It is, so to speak, the smallest coin in chemical currency. A *molecule*, on the other hand, is the *smallest particle of a substance, elementary or compound, which can exist in the free state*.

In some cases, in the case of argon and of helium, for example, the atoms of an element can exist in the free state; and the atom and molecule, therefore, mean the same thing. In many cases, however, the free atoms of an element combine together to form aggregates of like atoms, so that the molecule of the element, or the smallest particle of the element capable of free existence, may consist of two or three or even of four atoms combined together.

The atomic theory of Dalton, modified by the molecular postulates of Avogadro, was found to be in harmony with all the known facts. It co-ordinated and explained these facts

and the laws of definite and multiple proportions; and it guided the course of investigation in chemistry and physics during the nineteenth century. On the basis of Dalton's theory, the great and wonderful superstructure of modern chemistry was largely built up. Facts, however, began to be encountered which could not be explained by Dalton's theory, and although this theory may still, perhaps, suffice for most practical purposes, it no longer gives a satisfactory picture of the constitution of matter. The atomic theory has not been discarded, but it has undergone, more especially during the present century, a remarkable evolution, the nature of which will be discussed in a later chapter.

**Symbols, Formulæ and Equations.**—From the earliest times, when the need or desire arose of recording the behaviour of substances, some form of symbolism or shorthand notation has been employed. Under the influence of Chaldean astrology, the belief arose that metals, the most important substances known in ancient times, owe their special properties to the planets, and the ancient astronomical signs for the planets were therefore used to denote the seven known metals, as shown in the following list :

<i>Metal.</i>	<i>Planet.</i>	<i>Sign.</i>
Gold	Sun	☉
Silver	Moon	☾
Copper	Venus	♀
Iron	Mars	♂

<i>Metal.</i>	<i>Planet.</i>	<i>Sign.</i>
Lead	Saturn	♄
Tin	Jupiter	♃
Quicksilver	Mercury	☿

The early alchemists, under the influence of the mysticism and obscurantism of the Alexandrian epoch, used a symbolic and mystical language in which their descriptions of alchemical operations were "wrapp'd in perplexed allegories." Metals were referred to not only by the names of the planets but also by the names of animals—the green dragon (mercury), the crow (lead or black sulphides), the red lion (cinnabar or gold), yellow scorpion (sulphur), etc. Chemical operations, also, were represented by allegorical pictures, such as a lion devouring the sun (Fig. 5), which



FIG. 5.—Allegorical representation of the solution of gold by aqua regia.

represented the solution of gold by *aqua regia*, or a salamander being heated on a fire, which represented the purification of gold by fire.

This fantastic and mystical allegorical symbolism was doubtless used by these early alchemists to give an air of wisdom and mystery to their writings; they were employed not so much to reveal as to conceal thought, and to make the writings unintelligible to the uninitiated.

By the later alchemists and by the chemists of the eighteenth century, attempts were made to extend the old astrological symbols and to make them more systematic. Thus the four elements of Aristotle were represented by the symbols :



Fire.



Water.



Air.



Earth.


The acids, *aqua fortis* (nitric acid) and *aqua regia* (mixture of nitric and hydrochloric acids), were represented by the symbol for water combined, in the form of a monogram, with the letters F and R respectively. Thus,



Aqua fortis.



Aqua regia.

Sulphur, which burns and forms an acid substance, was represented by the symbol, , which is a combination of the symbol for fire and the symbol for an acid, | . The symbol,













, a combination of the symbol for air and that for acid, and denoting, therefore, an acid obtained from air, was used to represent "nitrous air" or nitric oxide.

Although the symbols just referred to formed an intelligible if somewhat too elaborate shorthand, a much fuller and more definite meaning could be given to the symbols only after the introduction of the atomic theory by Dalton. The symbolic notation devised by Dalton was intended to represent not only definite proportions by weight of the elements, but also the qualitative and quantitative composition of compounds. In Dalton's system, elements were represented by circles carrying some distinctive mark, and compounds were represented by



groups of such circles, so as to indicate the composition, as is shown in the following table :

Hydrogen .		Iron . . .	
Oxygen . .		Zinc . . . .	
Carbon . .		Water . . .	
Nitrogen .		Carbon dioxide .	
Sulphur .		Alcohol . . .	

This pictorial symbolism, although it was doubtless useful in the early days, was both crude and cumbersome ; and difficulties soon arose when it became necessary to find a distinctive mark for each element. Dalton, indeed, had to have recourse to the simple expedient, already used by others some years previously, of labelling the circles by means of the initial letter of the name of the element, as in the case of iron and zinc. Obviously, however, it would be much simpler to leave out the circle altogether, and this was done, in 1811, by the distinguished Swedish chemist, BERZELIUS, to whom we owe the simple and convenient system of notation universally in use at the present day.

JONS JAKOB BERZELIUS was born at Westerlösa, in Sweden, in 1779, and after leaving school entered the University of Upsala as a student of medicine. Devoting himself to chemistry, in which he had, even at an early age, manifested great interest, Berzelius rapidly rose to a position of great distinction, and for many years occupied the Chair of Chemistry at the Medico-chirurgical Institute, Stockholm. A brilliant experimentalist, Berzelius greatly enriched the different departments of chemistry by the large number of important investigations which he carried out, and, more especially perhaps, by his determinations of atomic weights. By no means the least valuable contribution to chemistry which we owe to Berzelius is his system of chemical notation which he hoped—justifiably, as the future proved—“ might facilitate the expression of chemical proportions, show briefly and clearly the number of elementary atoms in each compound and, after the determination of their relative weights, present the results of each analysis in a simple and easily retained manner.”

Through his *Text-book of Chemistry* and his other writings, Berzelius, who was a man of sound and cautious scientific judgment and of great honesty of character, exercised a very powerful influence on the development of chemistry in the early part of the nineteenth century. His great services to science were recognised by many learned Societies which bestowed their honours on him, and by his King, who ennobled him in



JÖNS JAKOB BERZELIUS.

1818 and created him a Baron in 1835. After a life of honour and great achievement, Berzelius died in 1848.

In the system of notation introduced by Berzelius, which was universally adopted and is in use at the present day, the initial letter of the name of the element is taken to represent the element, *e.g.* O for oxygen, N for nitrogen, H for hydrogen, etc. When the name of more than one element begins with the same letter, a second letter is added as a distinguishing mark, *e.g.* C for carbon, Cl for chlorine, Cr for chromium, etc. In order to render the symbols internationally acceptable, Berzelius used

the Latin or latinised names of those elements which were known to the Ancients, and which had acquired different names in the different countries. Thus, antimony (Lat. *stibium*) is represented by Sb; copper (*cuprum*) by Cu; gold (*aurum*) by Au; iron (*ferrum*) by Fe; lead (*plumbum*) by Pb; mercury (*hydrargyrum*) by Hg; potassium (*kalium*) by K; silver (*argentum*) by Ag; sodium (*natrium*) by Na; and tin (*stannum*) by Sn. These are the symbols which are shown in the table on p. 45.

If these symbols were to be regarded merely as abbreviations of the names of the elements, their use would doubtless be a matter of convenience, but they would have no scientific interest or value. They are, however, much more than a convenient shorthand, like the contractions Mr. for Mister, Dr. for Doctor, or Wm. for William; they have also a quantitative meaning, for each symbol represents not only the name of the element but one atom or one atomic proportion by weight of the element. The symbol O, for example, stands for 16.00 parts by weight of oxygen, and H, similarly, for 1.008 parts by weight of hydrogen, these two numbers, 16.00 and 1.008, being the atomic weights of oxygen and hydrogen respectively.

Atoms of oxygen and atoms of hydrogen, however, do not exist in the free state under ordinary conditions. There are grounds for believing that when the atoms of these elements are liberated from compounds, they combine *in pairs* to form *molecules* of oxygen and of hydrogen, the molecule being the smallest particle of a substance capable of existing in the free state. To represent the molecule of oxygen, therefore, one writes O<sub>2</sub>, the numeral which indicates the number of atoms in a molecule being written as a suffix below the line. The symbol O<sub>2</sub> represents, then, one molecule or one molecular proportion (two atomic proportions) by weight of oxygen. In the case of phosphorus, the molecule consists of four atoms, and its symbol is therefore, P<sub>4</sub>.

Since a compound is regarded as being formed by the combination of atoms, one can conveniently represent the molecule of a compound by writing the symbols of the constituent atoms side by side. Thus, NaCl represents a compound of sodium and chlorine, the molecule of which contains one atom of sodium and one atom of chlorine. But NaCl is the *formula*,<sup>1</sup> as it is called, of the compound sodium chloride, which is the chemical name for common salt. This formula, moreover, tells us that one molecular proportion of common salt contains one atomic proportion, or 23 parts, by weight of sodium, and one atomic

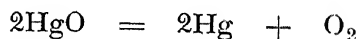
<sup>1</sup> One speaks of the symbol of an element and the formula of a compound.

proportion, or 35.46 parts, by weight of chlorine. One molecular proportion of sodium chloride, therefore, represents 58.46 parts by weight of the compound. In other words, if the mass of the oxygen atom is represented by 16.00, the mass of the molecule of sodium chloride is 58.46. *The molecular weight of a compound*, therefore, being equal to the sum of the atomic weights of the elements forming it, *is the weight of a molecule of the compound relatively to the weight of an atom of the standard element.*

In the case of sodium chloride the molecule is formed by the combination of one atom of sodium and one atom of chlorine, but, frequently, the molecule of a compound is formed by the combination of elements in more than one atomic proportion. In the case of water, for example, two atoms of hydrogen unite with one atom of oxygen to form a molecule of the compound; and so one writes the formula of water  $\text{H}_2\text{O}$ . The formula  $\text{NH}_3$ , similarly, which is the formula of ammonia, indicates that the molecule of this compound contains three atoms of hydrogen united with one atom of nitrogen, and the formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , which represents a molecule of sucrose (cane sugar), indicates that the molecule of this compound is formed by a group of twelve atoms of carbon, twenty-two atoms of hydrogen and eleven atoms of oxygen.

In this symbolic language of the chemist there is nothing mystic or mysterious; it has been devised not for the purpose of leading undesirably inquisitive people astray, but of facilitating the study and understanding of chemistry by conveying a large amount of information in a clear and concise manner. For the serious student of chemistry a knowledge of the language is essential and is readily gained by use; on the other hand, the layman must beware of mistaking a memorised knowledge of a number of symbols and formulæ for an understanding of the science.

By means of the symbols of elements and formulæ of compounds, one is also enabled to represent very clearly and concisely the results of a chemical change or chemical reaction. Thus, we learned that when red oxide of mercury is heated, decomposition takes place with production of oxygen (a gas) and of mercury. This fact can be represented thus:



Translated into words, this *chemical equation*, as it is called, reads thus: Two molecules (or molecular proportions by weight) of oxide of mercury yield, on decomposition, two molecules, or

atoms, (or two molecular or atomic proportions by weight) of mercury and one molecule (or molecular proportion by weight) of oxygen. In accordance with the law of indestructibility of matter or conservation of mass, the sign of equality indicates that the number of any particular kind of atom, and also the total mass, on either side is the same. On the left-hand side, there are two molecules of oxide of mercury, and since each molecule consists of one atom of mercury and one atom of oxygen, there are, altogether, two atoms of mercury and two atoms of oxygen. On the right-hand side, similarly, we have two atoms of mercury and of oxygen.

Moreover, the formula,  $\text{HgO}$ , indicates that 200.6 parts by weight (one atomic proportion) of mercury are combined with 16.00 parts by weight of oxygen to give 216.6 parts (one molecular proportion) of mercuric oxide. The above equation, therefore, informs us that  $2 \times 216.6$ , or 433.2, parts by weight of mercuric oxide yield on decomposition  $2 \times 200.6$ , or 401.2, parts by weight of mercury and 32.0 parts by weight of oxygen. By means of the symbols and formulæ, therefore, one is enabled to represent not merely what are the products of chemical change but also the proportions by weight of the different substances involved in the change. Thus, since 433.2 parts by weight (grams, pounds, tons, etc.) of mercuric oxide give 32 parts by weight (grams, pounds, tons, etc.) of oxygen, one can calculate how much oxygen would be obtained by the decomposition of any given amount of the oxide.

A knowledge of these quantitative relations is of the highest importance not only from the theoretical but from the practical and industrial point of view, for by means of the chemical equations and the atomic weights of the elements, one can calculate the maximum "yield" of a product which can be obtained from a given amount of the raw material. This theoretical maximum is never reached, owing to unavoidable losses of one kind or another, but a knowledge of the theoretical maximum will direct attention to these losses and indicate their magnitude.

**Valency.**—Although atoms can combine with one another to form a compound or compounds, it has been established as the result of many experiments, that the power or capacity of any given atom to combine with some other atom is not unlimited. The atoms of two different elements may combine in more than one proportion, but not in every proportion. Sodium and chlorine, for example, can combine only atom for atom, to form the compound sodium chloride, represented by the formula

NaCl. The sodium atom, however, cannot combine with two or three or more atoms of chlorine to form such compounds as  $\text{NaCl}_2$ ,  $\text{NaCl}_3$ , etc. Hydrogen, similarly, can combine with chlorine only atom for atom to form the compound known as hydrogen chloride, HCl. On the other hand, the metal calcium can combine with two (and only with two) chlorine atoms to form the compound calcium chloride,  $\text{CaCl}_2$ ; aluminium can combine with three chlorine atoms to give  $\text{AlCl}_3$ ; and carbon can combine with four chlorine atoms to form  $\text{CCl}_4$ . The atoms of the different elements, therefore, have a certain combining capacity, or have a certain *value* or worth, as measured by the number of atoms of another element with which one atom of the given element can combine. This combining capacity or value is called the *valency* or *valence*<sup>1</sup> of the element. Since one atomic proportion of hydrogen is never known to combine with more than one atomic proportion of any other element, the combining capacity or valence of hydrogen is taken as the standard and put equal to unity. Hydrogen is said to be a *univalent* element. Similarly, an element which combines with hydrogen, atom for atom, or which can take the place of one atom of hydrogen, is also said to be univalent. Thus, chlorine, which forms with hydrogen the compound HCl, is univalent; and sodium, one atom of which can take the place of one atom of hydrogen, as shown by the formulæ HCl and NaCl, also is univalent. Oxygen and sulphur, on the other hand, are *bivalent*, for one atom of these elements can combine with two atoms of hydrogen to give  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ ; nitrogen is *trivalent*, as shown by the formula for ammonia,  $\text{NH}_3$ ; and carbon, which forms the compounds  $\text{CH}_4$  and  $\text{CCl}_4$ , is *quadrivalent*.

Since a number of the elements do not form compounds with hydrogen, it is not possible in their case to define the valence in terms of their capacity to combine with that element. It may, however, be defined in terms of capacity to combine with some other univalent element, or with another element, *e.g.* oxygen, the valence of which is known. Thus, summing up, one may say: *The valence of an element is equal to the number of atoms of hydrogen, or other univalent element, with which one atom of the given element can combine; or is equal to twice the number of atoms of oxygen, or other bivalent element, with which one atom of the given element can combine.*

The fact that elements can combine in more than one proportion is an indication that the valence of an element has not a constant, unchangeable value. The valence may vary up to

<sup>1</sup> From the Latin *valere*, to be worth

a certain maximum value according to the conditions of experiment. In the series of compounds, for example, which nitrogen forms with oxygen (Chap. XXIII), the valence of the nitrogen varies from one to five.

That elements have a limited combining power or valence was first clearly stated by E. FRANKLAND (1825–1899)<sup>1</sup> in 1852; and some years later, on the basis of this doctrine, chemists began to indicate, by means of lines or “bonds,” the mutual attachments of the atoms within the molecule, each “bond” representing one valence. In this way one obtained what are known as *graphic* formulæ, *e.g.*  $\text{H}-\text{Cl}$ ,  $\text{H}-\text{O}-\text{H}$ ,  $\text{O}=\text{C}=\text{O}$ . The introduction of graphic formulæ was an event of the greatest historical interest and importance, for by means of these formulæ chemists attempted for the first time to visualise the inner structure of the molecule and the arrangement of the atoms relatively to one another. The use of these formulæ was developed with great success, more especially by the German chemist Kekulé, for the formulation of the very numerous series of compounds of carbon, so that there has developed a veritable architecture of the molecules. The story of some of the remarkable achievements in this field will be told later.

The doctrine of valency was put forward as an empirical doctrine; a conclusion drawn from experiment and uninterpreted by theory. It was descriptive rather than explanatory; it indicated a limitation of the combining power of elements and it imposed a check on the formulation of the compounds formed, but it threw no light on the underlying reality of atomic nature of which such a limitation of behaviour is a manifestation. On the doctrine of valency the atomic theory of Dalton also threw no light; and it is only in recent years that one has found its theoretical basis in that conception of the electronic constitution of the atom which we owe mainly to the physicists of the twentieth century. To a discussion of this we shall proceed in a later chapter.

<sup>1</sup> Professor of Chemistry at the Royal Institution and at the Normal School of Science and Royal School of Mines, London. Created Knight Commander of the Bath (K.C.B.) in 1897.

## CHAPTER V

### ATOMIC WEIGHTS AND THE PERIODIC LAW

SINCE the atomic hypothesis which was promulgated by Dalton in the early years of the nineteenth century postulated that the atoms have definite weights or masses, it became a matter of importance to determine the atomic weights or the relative weights of the atoms of the different elements. Although the experimental investigation of the proportions in which elements combine was actively pursued, more especially by Berzelius, confidence in the accuracy of the atomic weights calculated therefrom was long delayed; and it was not till about 1860, as we shall learn more fully later, that chemists recognised in the molecular theory propounded by Avogadro in 1811, a sure basis on which to found their calculations of atomic weights.

The values of the atomic weights, determined with greater accuracy and definiteness on the basis of Avogadro's theory, served not only as the foundation of quantitative chemistry but also as the basis of a classification of the elements which has exercised an extraordinarily great influence on the development of the science.

Even as early as 1829, JOHANN WOLFGANG DÖBEREINER (1780–1849), Professor of Chemistry at Jena, published an account of certain relationships which he had found to exist between the atomic weights of certain analogous elements, or elements of similar chemical properties. Döbereiner found that it was possible, in a number of cases, to form the elements into “triads,” or groups of three, the members of which were related to one another in such a way that the atomic weight of one was approximately equal to the mean of the atomic weights of the other two. For example, the elements lithium, sodium and potassium form such a triad, the atomic weight of sodium (23.0) being equal to the mean of the atomic weights of lithium (6.94) and potassium (39.10). Thus,

$$\frac{6.94 + 39.10}{2} = 23.02$$



Similar triads are: chlorine (35.46), bromine (79.92), iodine (126.9); calcium (40.07), strontium (87.63), barium (137.4); sulphur (32.06), selenium (79.2), tellurium (127.5).

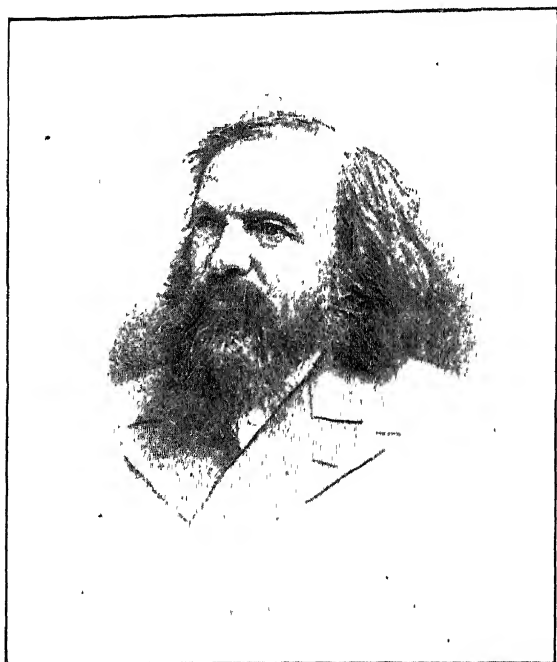
These regularities, which may possibly have been regarded as little more than arithmetical curiosities, had only a restricted application and aroused but a meagre interest among chemists; and it was not till 1868 and 1869 that LOTHAR MEYER (1830–1895), in Germany, and MENDELÉEFF, in Russia, discovered and elaborated the so-called PERIODIC LAW, which expresses in a comprehensive manner the relation between the general properties of the elements and their atomic weights. This law, which was first imperfectly perceived by the Englishman J. A. R. NEWLANDS in 1864 and called by him the law of octaves, may be stated in the form: *The properties of the elements and of their compounds are a periodic function of (or vary in a periodic manner with) the atomic weight*

DMITRI IVANOWITSCH MENDELÉEFF, by whom the periodic classification of the elements was most fully worked out and the inferences from it most clearly drawn, was, like Robert Boyle, the fourteenth child of his parents. Born at Tobolsk, in Siberia, in 1834, Mendeléeff became, in 1866, Professor of Chemistry at the University of St. Petersburg, where he carried out many important investigations, more especially on the properties of solutions. Coming into conflict with the University authorities owing to his sympathy with what were regarded as too liberal political views and to his “irreconcilable enmity” to the classical system of education then in vogue, Mendeléeff retired from his professorship in 1890. In 1893, he was appointed Director of the Bureau of Weights and Measures, and this post he held till he died in 1907. One of the foremost chemical philosophers of the nineteenth century, Mendeléeff’s genius and service to science were recognised alike by learned societies and by universities, which bestowed their honours on him. “In appearance, Mendeléeff was a genuine Slav. Medium in height, rather powerfully set, with an abundance of hair reminding one of a Paderewski, expressive blue eyes, high cheek bones, an immense forehead, he commanded attention wherever he went.”<sup>1</sup>

From a study of the atomic weights of elements known at the time, Mendeléeff was struck by the fact that when the elements are arranged in the order of their atomic weights, a remarkable recurrence of properties is observed. This periodicity

<sup>1</sup> Harrow, *Eminent Chemists of our Time* (T. Fisher Unwin).

or periodic variation of properties was very noticeable in respect of the general chemical behaviour and of the valence of the elements; for, when the elements were arranged in order of ascending atomic weights and in accordance with the valence, it was found that they fell into a number of groups or families of related elements or elements having analogous properties. In this way a natural classification of the elements was achieved,



DMITRI IVANOWITSCH MENDELÉEFF.

a classification depending on the relation between the chemical properties of the elements and their atomic weights.

In order that related elements might fall into the same group, it was necessary to leave a number of gaps in the table of elements, gaps which Mendeléeff predicted would one day be filled through the discovery of elements unknown at that time. Moreover, with the confident daring which comes from a recognition of the value and meaning of a scientific law, Mendeléeff predicted the properties which those elements would be found to possess when they were discovered. Thus, in the case of one of these unknown elements which Mendeléeff called "ekasilicon," the properties which he foretold in 1871 were found, with what

one may rightly regard as an astounding degree of accuracy, in the element germanium which was discovered in 1886 by the German chemist CLEMENS ALEXANDER WINKLER, Professor of Chemistry at Freiburg. The following table gives the comparison :

	" Eka-silicon "	Germanium
Atomic weight . . . . .	72	72.6
Specific gravity . . . . .	5.5	5.469
Specific gravity of oxide . . . . .	about 4.7	4.703

Although, as we shall presently learn, certain anomalies are met with in the Mendeléeff classification, anomalies which have in recent years received an explanation, the periodic law has served to co-ordinate the different elements and to bring order and harmony into what would otherwise have been a disarray of isolated facts; and to the guidance which it has given in investigation we owe the discovery of many new elements, chief among which are the so-called rare gases, helium, neon, krypton and xenon. As Mendeléeff himself said in the Faraday Lecture delivered in 1889 before the Chemical Society in London: "Before the promulgation of the periodic law the chemical elements were mere fragmentary, incidental facts in Nature; there was no special reason to expect the discovery of new elements, and the new ones which were discovered from time to time appeared to be possessed of quite novel properties. The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision; and long ere they were discovered new elements appeared before our eyes possessed of a number of well-defined properties."

On approaching the study of the elements as known at the present time, one finds that hydrogen occupies an unique position at the head, so to speak, of the rank and file of the elements. Leaving this element out of account for the present, therefore, and writing the other elements in ascending order of atomic weights, we have what are called the elements of the first period, namely,

Helium.	Lithium.	Beryllium.	Boron.	Carbon	Nitrogen	Oxygen.	Fluorine
4.00	6.94	9.02	10.82	12.00	14.01	16.00	19.00

This is followed by the second period of elements,

Neon.	Sodium.	Magnesium.	Aluminium	Silicon.	Phosphorus.	Sulphur.	Chlorine.
20.2	23.0	24.32	26.97	28.06	31.03	32.06	35.46

These elements of the second period possess, member by member, properties analogous to those of the elements of the first period; that is, neon is similar to helium, sodium to lithium, magnesium



the two short and typical periods, each begins with a chemically inert gas which has not, so far, been found to form any compound and may therefore be regarded as having a valence of nought. Second in the period comes a highly reactive metallic or electro-positive<sup>1</sup> element having a valence of one, and this is followed by elements having a maximum valence, in the case of their compounds with oxygen, increasing from 2, as shown by beryllium and magnesium, to a valence of 7, as shown by fluorine and chlorine. In the case of the compounds with hydrogen, however, the valence rises to 4 in carbon and silicon and falls again to 1 in fluorine and chlorine. In the longer periods a similar variation of valency is also found, but the relations now become more complicated and cannot be discussed here.

Owing to the periodicity of properties, elements of similar or analogous character fall into corresponding places in the various periods. In the table of elements shown on the opposite page, the members of these "natural families" or groups of related elements, are joined together by full-drawn lines. Thus, the rare gases (helium, neon, argon, krypton and xenon) occupy a position at the beginning of each period; the so-called "alkali metals" (lithium, sodium, potassium, rubidium and caesium) come second in the period, whereas, at the end of the periods, there stand the "halogen" elements (fluorine, chlorine, bromine and iodine). The dotted lines join elements which are related to each other in certain respects, although not so closely as the members of the "natural families" just mentioned.

Within these natural families, also, one finds a gradation of properties with increase of atomic weight. The melting point, for example, of the alkali metals falls as the atomic weight increases, as the following values show: lithium, 186° C.; sodium, 97.5° C.; potassium, 62° C.; rubidium, 38° C.; caesium, 26° C. The colour of the halogen elements, also, varies from a pale yellow, in the case of fluorine, to a pronounced greenish-yellow, in the case of chlorine, a deep brown in the case of bromine and a dark purple in the case of iodine. It was, of course, by reason of such variations of properties within a family of related elements, as well as by reason of the variation of properties (valence, atomic weight, etc.), on passing from element to element within a period, that Mendeléeff was able, with such success, to predict the properties of undiscovered elements.

Although one must bear in mind that the periodic classification does not summarise the whole of chemistry nor perfectly reflect the properties of the elements, yet the periodicity of

<sup>1</sup> The significance of this term will appear later.

behaviour, the successful prediction of the properties of unknown elements and the way in which the many new elements which were afterwards discovered fell naturally, as it were, into their appointed places within the framework of the periodic classification, established the periodic law in an unassailable position. Thereby, however, as Lord Salisbury remarked,<sup>1</sup> the mystery which hangs over the elements was thickened rather than dissipated. "The discovery of co-ordinate families dimly points to some identical origin, without suggesting the method of their genesis or the nature of their common parentage." How, then, shall one explain this very remarkable law, and where shall one find the thread that binds the different elements into an ordered group?

Mendeléeff, it may be said, scorned all search for a common parentage and protested, in his Faraday Lecture already referred to, that "the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements, than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis." Mendeléeff's desire to emphasise the solidity of the experimental basis of the periodic law and his contempt of the "torments of classical thought" doubtless led him to forget that the aim of science is not merely to order nature and to find the law that binds together facts of a like kind, but, through imagination, to rise above the facts and to get a glimpse of the eternal and underlying truth of which the law is but a partial expression. Certain it is that speculation and investigation concerning the genesis of the elements were greatly stimulated by the recognition of the essential validity of the periodic law; and the evidence which had been accumulating during the nineteenth century has culminated in the experimental investigations of the twentieth, and in the theory of the electronic constitution of matter by means of which the periodic law receives interpretation. According to this well-established theory, the atom of the chemist, the unit of chemical exchange, can no longer be regarded as the unit of subdivision of matter, but is a complex structure built up of much smaller particles the nature of which is the same for all elements. To a discussion of this we shall proceed in the next chapter.

<sup>1</sup> Presidential Address to the British Association, 1894.

## CHAPTER VI

### RADIOACTIVITY AND ATOMIC CONSTITUTION

THE recognition by chemists of the essential validity of the periodic law and the indications which this law gave of the close interconnection of the elements—perhaps, even, of a common origin and parentage—aroused afresh interest in investigations and discussions relating to the nature of the atom and the problem of the constitution of matter. To Dalton, as to Newton, the atoms were “solid, massy, hard, impenetrable particles,” incapable of subdivision, and forming distinct and separate individuals, primordial and unalterable. Throughout the nineteenth century, however, the old Aristotelian idea of a unique matter, a *prima materia*—that “relic of the torments of classical thought,” as Mendeléeff called it—was repeatedly revived, and first of all, perhaps, by the physician and physiological chemist, WILLIAM PROUT (1785–1850), who graduated Doctor of Medicine at Edinburgh in 1811 and afterwards lectured on chemistry in London.

**Prout's Law.**—On examining the early and not very accurate determinations of atomic weights, Prout was impressed by the fact that most of the values, when referred to the atomic weight of hydrogen as unity, were either whole numbers or very nearly whole numbers. He therefore put forward the view that the protyl or *prima materia* of the ancients is hydrogen, and that the atoms of different substances are made up of various amounts of this primordial matter. The “sagacious speculation” of Dr. Prout, however, did not meet with general acceptance because the more accurate determinations of atomic weights, as carried out by Berzelius, and, later, in 1860, by the Belgian chemist Stas, whose work will remain for all time a model of care and accuracy, clearly showed that the deviation of the atomic weights of a number of the elements from whole multiples of the atomic weight of hydrogen could not be explained as due to experimental error.

During the last quarter of the nineteenth century little interest was shown in Prout's law, but many chemists, while

not accepting the validity of the law, were not prepared to subscribe to the declaration of Stas that the law of Prout must be considered as *une pure illusion*. The feeling, indeed, persisted that the law contains an element of truth; and this feeling was strengthened when, in 1901, the Hon. R. J. STRUTT, now Lord RAYLEIGH, pointed out that "a calculation of the probabilities involved confirms the verdict of common sense, that the atomic weights" (referred to that of oxygen equal to 16.00) "tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence. The chance of any such coincidence being the explanation is not more than 1 in 1000, so that . . . we have stronger reasons for believing in the truth of Prout's law than in that of many historical events which are universally accepted as unquestionable." How strongly the "verdict of common sense" has been confirmed by the epoch-making investigations of the twentieth century, and how nearly the hypothesis of Prout agrees with present-day views regarding the constitution of the atom, it shall now be our business to consider.

**Cathode Rays.**—The new light which, during the present century more especially, has been shed on the problem of the

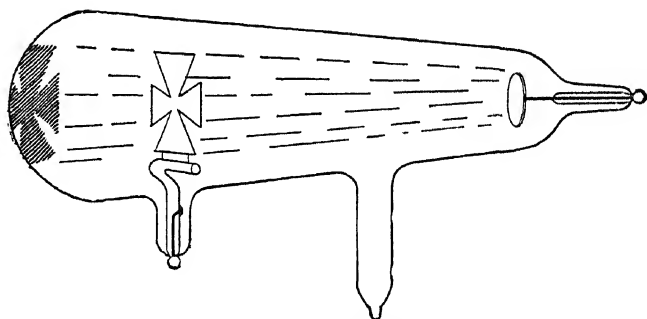


FIG. 7.—Crookes tube.

constitution of matter, came first from an unexpected direction, namely, from a study of the discharge of electricity through highly rarefied gases. In 1859, it was discovered by the German physicist, JULIUS PLÜCKER (1801–1868), that when an electric discharge is allowed to take place in a highly evacuated glass tube, a peculiar radiation is projected from the negative electrode or *cathode*, as it is called; and this radiation excites a phosphorescent light in the glass of the tube opposite to the cathode. This radiation, moreover, known as the *cathode rays*, travels in straight lines, and if a solid object is placed in the path of the rays, a shadow is cast (Fig. 7). A wheel, also, may be caused



to rotate by allowing the cathode rays to strike against its vanes, and a number of minerals, such as kunzite,<sup>1</sup> zinc sulphide and willemite (zinc silicate), glow with a phosphorescent light when bombarded by the cathode rays. Moreover, by using a concave cathode, whereby the rays can be brought to a focus, a metal, placed at the focus, can be raised to incandescence or even melted under the fury of the bombardment by the cathode rays, the nature of which was first clearly proved by Sir JOSEPH J. THOMSON.<sup>2</sup>

Although it had been surmised by the late Sir WILLIAM CROOKES (1832-1919), even as early as 1879, that the cathode rays are composed of small particles or corpuscles, proof of this was obtained only in 1897 by Sir J. J. Thomson. That the cathode rays are the carriers of negative electricity was already known from the fact that they are deflected in a particular manner by a magnet; and Thomson, by ingenious and careful experiment, determined the amount of the charge on the particles, the mass of the particles and the velocity of their flight. The negatively charged particles constituting the cathode rays, he found, travel with the enormous velocity of from 10,000 to 100,000 miles per second, the latter velocity being such that the particles would encircle the earth four times in the space of a second.

The mass of these negatively charged particles or *electrons*, as they are now called, is exceedingly small and equal to one eighteen-hundred-and-thirtieth ( $\frac{1}{1830}$ ) of the mass of the hydrogen atom, the lightest atom or lightest particle of matter hitherto known.<sup>3</sup> In this way, the existence of particles very much smaller than the chemical atom was discovered. The electron, moreover, may be regarded as the unit of negative electricity, for no charge less than that associated with an electron has been obtained.

Investigation has shown that electrons can be produced in

<sup>1</sup> This is a variety of spodumene, which has the composition of a lithium aluminium silicate.

<sup>2</sup> Joseph John Thomson, now Master of Trinity College, Cambridge, was born near Manchester in 1856. When not yet twenty-eight years of age, he was elected Cavendish Professor of Experimental Physics in the University of Cambridge. He was awarded the Nobel Prize in Physics in 1906, was created a Knight in 1908, and was awarded the British Order of Merit in 1912. While in charge of the Cavendish Laboratory he built up a School of Research the fame of which has never been surpassed.

<sup>3</sup> Since the mass of the hydrogen atom has been calculated to be  $1.64 \times 10^{-24}$  gram (i.e. 1.64 divided twenty-four times by 10), the mass of the electron is only  $9.0 \times 10^{-28}$  gram. In other words, it would take about one quadrillion, or one million million million million atoms of hydrogen to make up the weight of 1 gram (15.4 grains). (For the relation between grams and other units of weight, see Appendix.)

various ways : by the electric discharge as cathode rays ; by the action of ultra-violet light on metals ; and by raising metals to incandescence, as in the " valve " used in wireless telephony. In all cases, however, the particles or electrons are the same, and therefore the electron must be a constituent of many different substances. From this consideration there arose the conception of the electronic constitution of matter or of the atom.

From another direction, also, further impressive evidence was soon obtained that the atom is no longer to be thought of as a single, indivisible, unchangeable particle, but as a vibrant microcosm, a complex system, capable of undergoing, in certain cases at least, an amazing and spontaneous transformation into atoms of a different kind.

**Radioactivity.**—In 1895, it was found by the German physicist, WILHELM KONRAD VON RONTGEN (1845–1923), that when

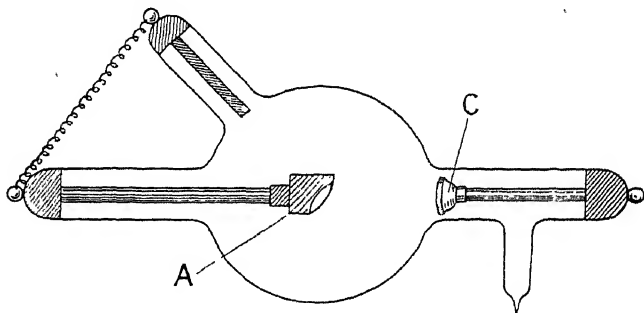


FIG. 8.—X-ray tube.

The electrons projected from the cathode, C, impinge on the anti-cathode, A, whereby X-rays are produced.

the cathode rays are brought to a focus and allowed to impinge on a plate of a dense metal such as platinum (Fig. 8), rays are produced which can pass out through the glass of the tube and affect a photographic plate, and they can also render certain substances (*e.g.* barium platinocyanide) fluorescent. These rays, generally called X-rays, the use of which in surgery is so well known, are ethereal vibrations similar to the vibrations constituting ordinary light; but of very much shorter wavelength. In 1896, the French physicist, HENRI BECQUEREL (1852–1908), thinking that the X-rays might have their origin in the fluorescence produced in the glass by the cathode rays, placed a salt of uranium, which fluoresces when exposed to light, on a photographic plate protected from the action of ordinary light. After some time, Becquerel found, on developing the photographic plate, that the uranium salt had emitted a radiation

which had penetrated the wrapping and produced a dark patch on the plate. This result appeared, therefore, to confirm Becquerel's view regarding the origin of X-rays. On proceeding to repeat his experiment, Becquerel was interrupted, and he placed the protected photographic plate with uranium salt on it, in a dark cupboard, where it remained some days. As the uranium salt fluoresces only on exposure to light, Becquerel did not expect that any effect would be given by the salt which had been all the time in a dark cupboard. Nevertheless, he developed the plate, and was astonished to find that an image had been produced quite as dark as that which had been formed when the uranium salt was exposed to light. The action on the photographic plate could not, therefore, have been due to fluorescence. By this happy chance, Becquerel was led to the discovery that the compounds of uranium continuously and spontaneously emit "rays" or radiations which have the power of passing through wood, paper and other opaque materials, and of affecting a photographic plate in a manner similar to X-rays. In this way was discovered the property of *radioactivity*, a property which was found to be due not to the salt as a whole but to the uranium in the salt. In other words, radioactivity, as was shown later by Mme. Curie, is a property of the uranium atom.

It was found by Becquerel that the radiations which are emitted by radioactive substances have the property not only of penetrating paper and other materials opaque to ordinary light, but also of rendering the air a conductor of electricity; and this property has been of very great value for the measurement of the radioactive power of different substances. When a gold-leaf electroscope (Fig. 9) is charged with electricity, the gold leaves mutually repel each other to an extent which depends on the amount of the charge. In dry air, the leaves remain apart, because the air is a non-conductor; but if a radioactive material be brought near to the electroscope, the gold leaves fall together more or less rapidly, owing to the fact that the air is rendered conducting (or is *ionised*, as it is said). The electric charge is therefore conducted away and the gold leaves,

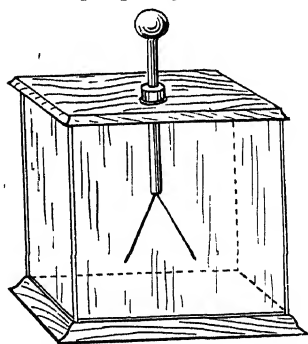


FIG. 9.—Gold-leaf electroscope.

A brass rod, carrying two strips of gold leaf attached to its end, passes through an insulating collar in the lid of a box with glass sides.

losing their charge, no longer mutually repel each other. The more powerfully radioactive the material, the more rapidly will the leaves come together.

The investigation of a large number of materials by Mme. CURIE,<sup>1</sup> wife of the late Professor PIERRE CURIE (1859–1906), at the Sorbonne in Paris, led to the discovery not only that the element thorium is radioactive, but that in the uranium-containing mineral, pitchblende, there existed a hitherto unknown element which, on account of its great radioactive power—more than a million times greater than that of uranium—received the name *radium*. Although present in pitchblende to the extent of only about 1 part in 10,000,000, this element was separated, by a long and laborious process, in the form of its salt, radium bromide, a white substance similar in appearance to common salt; and in 1910, Mme. Curie obtained metallic radium by electrolysing a solution of radium chloride. Its properties are similar to those of calcium.

At the present time, the deposits of uranium minerals at Katanga, in the Belgian Congo, constitute the main source of supply of radium, but the element is also obtained in notable quantities from the mineral, pitchblende, occurring at Joachimsthal, in Czechoslovakia. Radium is employed in the form of its salts, the bromide and chloride, and must, on account of its very great radioactive power, be handled with care; for if kept for a short time near the body, it cauterises the skin and produces a sore which is difficult to heal. It is used, to a considerable extent, in the treatment of cancer and other malignant growths.

The investigation of the radioactive elements, uranium, thorium and radium, has shown that they are continuously and spontaneously giving out positively and negatively charged particles, the so-called alpha ( $\alpha$ ) and beta ( $\beta$ ) rays; and they are the source, also, of ethereal vibrations, the gamma ( $\gamma$ ) rays, which are similar in nature to the X-rays. Like the X-rays, the gamma rays are highly penetrating, the thickness of layer passed through being all the greater the smaller the atomic weight of the substances. The beta rays, also, which consist of negatively charged electrons shot out from the atom with a velocity approaching that of light, have considerable penetrating power, but the alpha rays, which, as we shall presently learn,

<sup>1</sup> Marie Skłodowska, afterwards Mme. Curie, was born at Warsaw, Poland, in 1867. She succeeded her husband, in 1906, as Professor of Physics at the Sorbonne, Paris, and in 1919 was made Honorary Professor of Radiology in the University of Warsaw. She was awarded the Nobel Prize in Physics in 1903 and the Prize in Chemistry in 1911.

are positively charged helium atoms, are easily stopped by a sheet of note-paper. They are, of course, all stopped by the glass walls of the tube in which, ordinarily, the small quantities of radium salt are sealed up. These alpha rays, however, possess, by reason of their greater mass, much more energy than the electrons (beta rays), and are much more effective in breaking up or ionising the molecules of the atmospheric gases and so rendering the air a conductor of electricity.

The emission of alpha particles by a radium salt can be demonstrated very simply by means of a small apparatus, called a *spinthariscopes*, invented by Sir William Crookes. A small piece of a radium salt is supported on the tip of a wire fixed inside a metal tube at a short distance from a screen coated with zinc sulphide. On viewing the screen in the dark through a magnifying glass, which can be focussed on the screen by means of a sliding tube, scintillating flashes of light are observed, due to the bombardment of the screen by alpha particles, each impact being marked by a flash.

A beautiful experiment by C. T. R. WILSON, now Professor of Natural Philosophy in the University of Cambridge, enables one to trace the path of an alpha particle. A small particle of a radium compound is supported in a flask which contains air saturated with moisture. On cooling the air by rapid expansion, the ions or electrically charged particles into which the molecules of the atmospheric gases are broken by the alpha particles, act as condensation nuclei for the moisture, and the paths of the rays are traced in fog. With suitable illumination these fog-tracks can be photographed, and an appearance similar to that shown in Fig. 10 is obtained. The track of an alpha particle is, in most cases, a straight line or nearly a straight line, but occasionally, as the figure indicates, a sharp deflection is shown. The interpretation of this behaviour will be given later.

Although the scientific imagination of a Dalton had conceived the existence of atoms, chemists deal, in their reactions, not with single atoms but with enormous numbers of atoms. By means of the *spinthariscopes*, however, and the fog-tracks of alpha particles, we become witnesses of effects due to single, individual atoms of matter. The atomic hypothesis thereby gains an objective reality undreamt of by Dalton and the later chemists of the nineteenth century.

While the three most important radioactive elements are uranium, thorium and radium, electrical measurements have shown that these elements give rise to a large number of other radioactive elements which have a much more transient existence.

Thus, radium gives rise to a gas which was called by Ramsay niton, but which has now been rechristened radon. This gas is itself radioactive and can be observed, like radium, to glow in the dark. When the gaseous radon is removed from the original radium salt, it gradually loses its radioactivity and disappears; but just as fast as the separated radon disappears, just so fast is fresh radon produced by the original radium, spontaneously and always at the same rate, unaltered and uninfluenced by anything that man can do. Nor is this all. From the radium there is produced successively a whole series of radioactive substances: radium, radon, radium-A, radium-B,

y

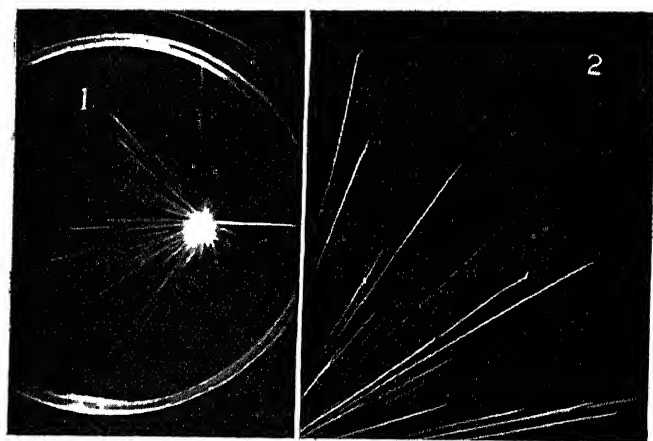


FIG. 10.—Fog-tracks of alpha particles.

1, tracks of alpha particles emitted by radium; 2, tracks of the particles, enlarged.

etc., down to radium-G, which is lead. These different members of a radioactive series, which are obtained, for the most part, only in unweighable amounts, are distinguished from one another and identified by the rate at which the radioactive power diminishes or "decays." Thus, the radioactive power of radium falls to half its value in a period of 1730 years, whereas the corresponding time for radon is 3.85 days, and for radium-A, 3 minutes.

While, as we have just seen, radium is the progenitor of a long line of descendants, it can itself also boast an ancient lineage, for the "first parent" of this series of radioactive elements is uranium, the element, as we have seen, in which the property of radioactivity was first detected. From uranium there are

formed, in succession, uranium- $X_1$ , uranium- $X_2$ , uranium-II, ionium, and it is this last-mentioned element, ionium, which, by the loss of an alpha particle, gives rise to radium.

The element thorium gives rise to a similar series of products, of which the final member is again lead.

One of the disintegration products of thorium, known as mesothorium-I, is now obtained in considerable quantities as a by-product of the incandescent gas-mantle industry. Mesothorium-I loses half its radioactivity in five and a half years, so that its life is comparatively short; but for that very reason highly active preparations can be obtained. The commercial mesothorium is largely employed in the manufacture of luminous paints, which can be applied, for example, to the hands of watches and so make it possible for the time to be read in the dark.

**Disintegration Theory of Radioactivity.**—Although the fact of radioactivity is now familiar to all, the phenomena of radioactivity were, in the closing years of the nineteenth century, startling in their unexpectedness, and they were bewildering and inexplicable until, in 1902, Sir ERNEST RUTHERFORD and Professor F. SODDY<sup>1</sup> put forward their now universally accepted hypothesis of atomic disintegration. According to this hypothesis, the atom of a radioactive element is a complex system of particles which undergoes spontaneous change, or explodes as it were, with projection, at a very high velocity, of negatively charged electrons (the beta rays), and of heavier, positively charged particles (alpha rays). Not all the atoms of a radioactive substance, however, undergo disintegration at one moment; only a certain definite fraction of the atoms reach the condition of instability at the same time. In the case of radium, for example, only about one out of every hundred thousand million breaks up each second; and the fraction is definite for each element. The greater the fraction, the more powerfully radioactive is the substance.

A striking confirmation of the correctness of the disintegration hypothesis of radioactivity and of the complexity of atoms was obtained when Sir William Ramsay and Sir Ernest Rutherford showed, by direct experiment and in different ways, that the positively charged alpha particle which is expelled from radioactive substances, is a positively charged helium atom,

<sup>1</sup> Sir Ernest Rutherford, O.M., President of the Royal Society and Cavendish Professor of Experimental Physics in the University of Cambridge, and Frederick Soddy, Professor of Inorganic and Physical Chemistry in the University of Oxford, were, in 1902, Professor of Physics and Demonstrator in Chemistry, respectively, in McGill University, Montreal.

or, as we shall learn more fully presently, a helium atom which has lost two electrons. Not only did Rutherford isolate the alpha particles and show that, on losing their electric charge by taking up electrons, they form ordinary helium, but he also succeeded in counting the number of alpha particles emitted by a given weight of radium, by allowing the particles to pass through a small hole and impinge on a fluorescent screen. At each impact of an alpha particle, a little flash of light was produced, and by counting the number of flashes the number of particles passing through the opening was obtained. Since the number of alpha particles expelled from a given weight of radium can be counted, and since each alpha particle becomes a helium atom, it is possible, by measuring the volume of helium produced by a given weight of radium in a given time, to calculate the number of helium atoms (or molecules) in a given volume of the gas. The number obtained by Rutherford, namely, twenty-seven trillion five hundred thousand billion ( $2.75 \times 10^{19}$ ),<sup>1</sup> in one cubic centimetre at 0° C., is, as we shall see later, in good agreement with the value deduced from measurements of an entirely different kind.

The results which have been obtained from the investigations of radioactivity gain greatly in interest from the fact that they may be employed to throw light on the problem of the age of the earth, or, at least, on the age of the rocks making up the crust of the earth. It has already been pointed out that the element, uranium, undergoes a succession of disintegrations and gives rise to a series of products of which the final member is lead. A uranium mineral, therefore, always contains lead, and if one determines the relative amount of uranium and lead in the mineral it is possible, from a knowledge of the radioactive changes, to calculate approximately the time which would be necessary for the given proportion of lead to be formed, and in this way an approximate lower limit of age is obtained. Thus, it has been calculated that the middle pre-cambrian pegmatites of Ontario, Texas, Colorado, Sweden and India, have an age of about 1000 to 1100 million years.

**Atomic Structure.**—The striking proof of the complexity of the chemical atom, which is afforded by electrical and radioactive phenomena, gave a great impetus to the formation of definite views regarding the inner structure or constitution of what was formerly thought of as indivisible. Since negatively charged electrons constitute, as we have seen, a part of the atom of different substances, and since the atom as a whole is

<sup>1</sup> A billion is here taken as a million million, and a trillion as a million billion.



electrically neutral, it follows that there must be an amount of positive electricity within the atom equal to the total negative charge carried by the electrons. At first, it was suggested by Lord Kelvin and by Sir J. J. Thomson that the atom might be conceived of as a uniform mass of positive electricity, throughout which the electrons are distributed like the currants in a cake ; but the fuller investigation of the properties of matter, and more especially of the passage of alpha rays through matter, showed that the positive electricity in the atom could not exist in a diffuse form, but must be highly condensed. Sir Ernest Rutherford, therefore, suggested that the positive electricity is concentrated in a very minute nucleus, in which also almost the whole mass of the atom is supposed to be resident, the mass of the electrons being, in comparison, negligibly small. Around this minute, positively charged nucleus, the negative electrons are supposed to be arranged in the form of concentric spheres, or to move in orbits, like a sun ringed round with planets. The suggestion made by Sir Ernest Rutherford was a brilliant inference from experimentally determined data, and has in general been confirmed by all later work.

And what is the nature of the positively charged nucleus ? The atoms of the radioactive elements emit, on disintegrating, alpha particles or positively charged helium atoms, as well as beta rays or negatively charged electrons. In the case of the heavy atoms of the radioactive elements, therefore, we seem to have a proof that the positively charged nucleus of the helium atom is one of the units of atomic structure ; but since the mass of the helium atom (or nucleus) is nearly four times that of the hydrogen atom, the helium nucleus must itself be regarded as complex. The conclusion, therefore, is reached, a conclusion which commends itself to the mind on account of its simplicity no less than by its harmony with experimental evidence, that the positively charged nucleus of the hydrogen atom, the lightest atom, is itself the unit of positive electricity. To this unit of positive electricity which constitutes the nucleus of the hydrogen atom, the name *proton* has been given.

While the nucleus of the hydrogen atom can be regarded as formed by a single proton, the nuclei of the other elements must be more complex structures, and consist of both protons and electrons. Thus, in the case of helium, the nucleus must contain four protons, because the mass of the helium atom is about four times the mass of the hydrogen atom. From the behaviour of the alpha rays, however, the conclusion must be drawn that the helium nucleus carries only two positive charges, and,

consequently, the four protons of the nucleus must be associated with two electrons, in order that the excess positive charge may be only two units. In the neutral atom of helium, the two positive charges on the nucleus will be balanced by two planetary electrons. In general, then, an atom is to be regarded as consisting of a positively charged, complex nucleus, made up of protons and electrons, round which revolve planetary electrons equal in number to the excess positive charge on the nucleus.

The structure of the atom which has just been sketched and which presents us with a model, as it were, of the atom as inferred from the results of experiment, can, of course, reflect only the state of knowledge at a particular time, and must be modified or replaced by some other model as knowledge widens and deepens. Even already, the electron is ceasing to be regarded as a minute, structureless particle, and the motion of an electron is becoming assimilated to the motion of a wave. Until knowledge has further developed, however, we may accept the model described above, as representing generally the structure of the atom.

The recent investigations in the domain of atomic and sub-atomic physics have extended enormously the limit of subdivision of matter; and have given a proof that the atom, far from being a single indivisible particle or closely compacted mass, is a very open-spaced system of particles, the diameters of which are very small compared with that of the system as a whole, or of the atomic domain as it is called. It has, indeed, been calculated<sup>1</sup> that the diameter of an electron is only about one forty-thousandth of the diameter of the atom, and the diameter of the proton is still less, being about one eighteen-hundredth ( $\frac{1}{1800}$ ) of the diameter of an electron. The structure of an atom of hydrogen, therefore, has been compared with that of the solar system, and it has been pointed out that since the diameter of the earth is one twenty-thousandth of the diameter of its orbit round the sun, we can think of an atom as a system in which the earth represents an electron circling round a nucleus (much smaller than itself), at a distance equal to twice the distance of the earth from the sun. The atom, therefore, is mainly void, a thing of specks and spaces—mainly spaces—and one can understand how an alpha particle can pursue a straight path *through* the atoms of matter, as shown by the fog-tracks in the experiment referred to on p. 81, and is only occasionally diverted by a near approach to or collision with the massive, positively charged nucleus. It is to such collisions with or

<sup>1</sup> The calculations rest to some extent on unverified assumptions.

repulsions by the positively charged nuclei of atoms that one attributes the sharp deflection which is seen in the fog-tracks of some of the alpha particles (p. 82). It was, moreover, very largely by a study of such deflections of the alpha particles in passing through a gas that Sir Ernest Rutherford was led to his conception of the structure of an atom.

From the preceding discussion it will be evident how very nearly the hypothesis of Prout agrees with the now generally accepted views regarding the constitution of the atoms of different elements. Although the atoms of the elements are not to be regarded as built up of hydrogen atoms, but rather of hydrogen nuclei (protons) and electrons, the idea underlying the two views is essentially the same.

The idea of the atomic or discontinuous constitution of matter which was no more than a speculation when put forward by Epicurus, was revived by Gassendi and Newton as a cosmic hypothesis. Through the genius of Dalton it was developed into a scientific theory, and the investigations of the twentieth century have proved it to be a fact. Meanwhile, also, our views regarding the ultimate units of matter have undergone a change. To quote the words of the eminent French physicist, Jean Perrin: "Atoms are no longer eternal, indivisible entities, setting a limit to the possible by their irreducible simplicity; inconceivably minute though they be, we are beginning to see in them a vast host of new worlds. . . . Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense."

Although, as a philosophical conception of the nature of matter, the atomic theory of Dalton, with its postulate of an indivisible atom, must be abandoned, yet it is important to bear in mind that in all ordinary chemical reactions and changes the complex structure of protons and electrons acts as an indivisible unit which cannot be broken up, except, possibly, in a few cases by non-chemical means. To this, reference will be made later.

**The Atomic Number.**—According to the interpretation of experimental data, as we have seen, the atom is regarded as being composed of a positively charged nucleus and of planetary electrons or units of negative electricity. Since the number of planetary electrons, on which the chief chemical and physical properties of the elements depend, is determined by and is equal to the number of excess positive charges on the nucleus, a knowledge of the latter is of great importance. One of the greatest advances, therefore, in recent years, in connection with

the problem of atomic structure, has been the identification of the number of excess positive charges on the atomic nucleus with the serial number or *atomic number* as it is called, of the element in the periodic classification as given on p. 72. Since for the determination of the serial or atomic number of an element, several methods are available, one is thereby enabled to ascertain the nuclear charge, and therefore also the number of planetary electrons in the atom.

The recognition that the properties of an element depend on its atomic number, or number of planetary electrons, rather than on the atomic weight of the element, enables one to take account of the anomalies occurring in the Mendeléeff classification, namely, that argon must, on account of its chemical properties, be placed before potassium, and similarly tellurium before iodine, although the atomic weights are in the inverse order. In most cases, the atomic numbers and atomic weights follow the same order, but not in every case; and for the periodic recurrence of chemical properties it is the atomic number which is of importance. The periodic law must therefore be restated in the form: *The properties of the elements are a periodic function of (or vary in a periodic manner with) the ATOMIC NUMBER.*

The existence of a series of integral atomic numbers throws important light on the number of elements still to be discovered. On arranging the elements serially in order of the atomic numbers, as in the table on p. 45, it is found that only two gaps occur, indicating that between hydrogen and uranium only two elements remain to be discovered. The periodic classification now acquires a fuller meaning and becomes not only a record of the races and families of the elements, but a census sheet of individuals; a veritable register from which we can make the roll-call of the elements.

**Isotopes.**—Determinations of atomic numbers have shown that to each element there may be given a whole number which represents its serial number in the list of elements, starting from hydrogen which has the atomic number 1, up to uranium which has the atomic number 92; and the important conclusion can be drawn that as one passes from element to element, ascending the series, there is, at each step, an addition of one unit of positive electricity to the nucleus and a corresponding increase in the number of planetary electrons. Hydrogen has unit nuclear charge and one planetary electron; helium has a nuclear charge of two, and two planetary electrons; while uranium, with its atomic number 92, has no fewer than ninety-two planetary electrons to balance a nuclear charge of ninety-two units.

The chemical properties of an element, we have seen, depend on the atomic number, that is, on the number of planetary electrons in the atom; and since the nucleus of the heavier elements is a complex structure, made up of protons and electrons, it is clear that if one proton and one electron are removed from the nucleus, the atomic weight will be reduced by unity (the mass of one proton), but the positive charge on the nucleus will be unaltered. That is to say, the atomic number or the number of planetary electrons will be unchanged. The modern theory of atomic structure, therefore, opens up the astounding possibility of the existence of elements which have the same atomic number (and are therefore chemically identical), but have different atomic weights.

The existence of such elements was first realised in the case of radioactive elements; a fact which is perhaps not surprising since radioactive change is associated with a disintegration of the nucleus. Thus, as Soddy first pointed out, the emission of an alpha ray from the nucleus of a radioactive element corresponds with a lowering of the atomic number by two units and a diminution of the atomic weight by four units, because the atomic weight of helium is 4, whereas its atomic number (positive nuclear charge) is 2. In the disintegration, for example, of radium to form radium-B, we have the series:

		radium	$\xrightarrow{\alpha\text{-ray}}$	radon	$\xrightarrow{\alpha\text{-ray}}$	radium-A	$\xrightarrow{\alpha\text{-ray}}$	radium-B
Atomic weight	.	226		222		218		214
Atomic number	.	88		86		84		82

The atomic number of radium-B, therefore, is the same as that of lead, but its atomic weight (214) is greater than the atomic weight of lead (207.2).

On the other hand, the emission of a beta ray (a negative charge), from the nucleus, will increase the atomic number (or positive charge) by one unit, but, owing to the negligible mass of an electron, will leave the atomic weight unchanged. On pursuing the investigation of the radium disintegration series farther, one finds the following series of changes:

		radium-B	$\xrightarrow{\beta\text{-ray}}$	radium-C	$\xrightarrow{\beta\text{-ray}}$	radium-C <sub>1</sub>	$\xrightarrow{\alpha\text{-ray}}$	radium-D
Atomic weight	.	214		214		214		210
Atomic number	.	82		83		84		82

		radium-D	$\xrightarrow{\beta\text{-ray}}$	radium-E	$\xrightarrow{\beta\text{-ray}}$	radium-F	$\xrightarrow{\alpha\text{-ray}}$	radium-G
Atomic weight	.	210		210		210		206
Atomic number	.	82		83		84		82

Radium-D and radium-G, therefore, with their varying atomic weights, have the same atomic numbers as radium-B and lead.

Elements which have the same atomic number (and therefore the same chemical properties), but different atomic weights, were called by Soddy, *isotopes*.<sup>1</sup> Radium-B and radium-D are therefore isotopes of lead.

Radium-G and also the final product of the radioactive disintegration of thorium have been identified with the element lead. They have all the same atomic number. On calculating, however, the atomic weight of the lead formed by the disintegration of radium, one finds the value 206, whereas the lead formed from thorium is calculated to have the atomic weight 208.4, a very different value. Soddy, therefore, made the bold prediction that investigation would show that the atomic weight of lead present in uranium minerals is greater than that of lead contained in thorium minerals, or, generally, that the atomic weight of lead will depend on its provenance. The prediction was amply proved correct, and atomic weight determinations carried out by some of the most accurate workers in England, America, France and Germany yielded values which varied from 206.08 to 207.694. One cannot, therefore, escape the conclusion that ordinary lead is a mixture of isotopes of different atomic weights, and that the atomic weight value, 207.2, is merely an average value.

The occurrence of isotopes is not confined to the products of radioactive disintegration, but is met with also in the case of many of the ordinary elements. By means of an electrical method devised by Sir J. J. Thomson and improved by F. W. Aston, of the University of Cambridge, it has been found possible to determine, with very considerable accuracy, the mass of the positive nuclei, and therefore the mass of the atoms of different elements. By this method of positive ray analysis, as it is called, Aston has shown that if the atomic weight of oxygen be represented by the number 16, *the atomic weights of all other elements are to be represented by whole numbers, e.g. the atomic weight of helium by 4, of carbon by 12, of nitrogen by 14, etc., values which, it is true, are identical with the atomic weights as determined by chemical methods.* In the case of those elements which yield fractional atomic weights when determined chemically, Aston has shown that the element, as it is obtained by the chemist, is not simple, but consists of a mixture of isotopes, the atomic masses of which are represented by whole numbers.<sup>2</sup>

<sup>1</sup> From the Greek *isos* (isos), the same, and *τόπος* (topos), place. The significance of the term is that isotopes occupy the same place in the periodic classification.

<sup>2</sup> Hydrogen with an atomic mass of 1.008 is an exception. There are also slight divergences in the case of other elements, the explanation of which cannot, however, be discussed here.

Thus, chlorine, the atomic weight of which as determined by chemical methods, is 35.46, was found to be a mixture of two isotopes having atomic weights of 35 and 37 respectively, mixed together in the proportion of 3 to 1. The two isotopes have the same number of planetary electrons (namely, 17), and are therefore chemically identical, but, in one case, the nucleus consists of 35 protons and 18 electrons, while, in the other case, it consists of 37 protons and 20 electrons. Similarly, argon, with an atomic weight of 39.88, is a mixture of isotopes having atomic weights of 36 and 40; and krypton (atomic weight = 82.92) is a mixture of no fewer than six isotopes, the atomic weights of which are 78, 80, 82, 83, 84 and 86.

Philosophically, it is clear, the claim can no longer be made that the atomic weights of the elements are fundamental constants, for the existence of isotopes, with their integral atomic weights, shows that the fractional atomic weights are merely average values for mixtures. And yet, for practical purposes, the atomic weight has lost little of its former importance in chemistry, for the simple reason that nature, apparently, mixes the isotopes in constant, or practically constant, proportions. Thus, chlorine, from whatever source it is obtained, shows no appreciable difference in the proportions in which its two isotopes are mixed. In the case of lead, it is true, which can be formed by the disintegration of different radioactive elements as well as in other ways, the values of the atomic weight (and therefore the proportions in which the isotopes are mixed) may vary considerably. So far as known, however, this behaviour is exceptional.

The possibility of obtaining the different isotopes of lead, or different mixtures of isotopes, compels us to accept the law of fixed proportions in chemical combination with a certain reserve; for, in the case of lead chloride, the proportion of lead to chlorine by weight will obviously depend on which isotope of lead is used. This fact, however, does not destroy the general validity of the law of fixed proportions.

**Electronic Constitution and Valency.**—The conception of an atom as a complex structure formed by a positively charged nucleus surrounded by planetary electrons furnishes a theoretical basis for the doctrine of valency, which, as we have seen, was put forward as an empirical doctrine descriptive of the combining capacity of atoms. As one passes from element to element, the number of positive charges on the nucleus, and therefore the number of planetary electrons, increases at each step, as we have seen, by unity; and as the number of planetary electrons increases, the orbits in which they are regarded as revolving,

group themselves on the surface of concentric spheres or shells. In chemical combination it is the electrons of the outermost shell that are involved.

Although differences of opinion exist as to the arrangement of the planetary electrons, the study of the properties of the elements has led to the generally accepted conclusion that the arrangements found in the case of the inert gases of the helium series are specially stable, and that in the case of all these gases, except helium, there are eight electrons in the outermost ring, forming what is known as an octet. That is, maximum stability and chemical inactivity are found when the outermost ring contains eight electrons. Such elements have zero valency.

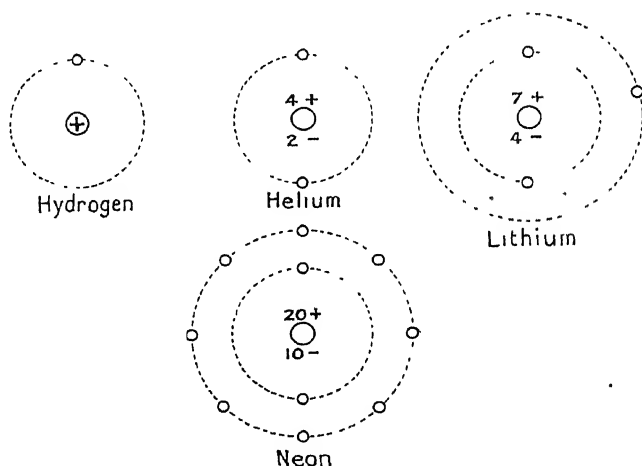


FIG. 11.—Diagrammatic representation of atomic constitution.

Helium, which has the atomic number 2, has two planetary electrons, and the system which is formed is presumably a very stable one. When, in the case of lithium, a third planetary electron is added, it does not enter into the already existing ring, which is very stable, but begins to form a new ring; and with each successive element, one electron is added to this second ring (Fig. 11). Thus, beryllium has two electrons in the outer ring, boron three, carbon four, nitrogen five, oxygen six, fluorine seven, neon eight. The octet is now complete; the system is one of maximum stability, and zero valence. On passing to the next element, sodium, with atomic number 11, a new ring of electrons is begun, and becomes complete in the case of argon, in which the electrons are arranged in three rings or shells containing respectively 2, 8 and 8 electrons. With



potassium, a fourth shell of electrons comes into existence ; and as one proceeds to elements of higher and higher atomic number, additional electrons are added to the ring. Complications, however, also begin to arise, the discussion of which would lead us too far.

The manner in which the planetary electrons are built up into shells, with a maximum of eight in the outermost shell, furnishes a physical basis for the doctrine of valency. Chemical combination can be regarded as due to the transfer of electrons from one atom to another and the production of electrostatic charges which bind the atoms together. In these reactions it is the electrons of the outermost layer which are involved, and valency can be regarded as an expression of the number of electrons which an atom must gain or lose in order to form a system with an outermost ring of eight electrons, or in order to assume the structure of the nearest inert gas. The sodium atom has one electron in its outermost shell, and it readily gives up this electron so as to form a positively charged system having the electronic constitution of neon. Chlorine, on the other hand, which has seven electrons in its outermost shell, readily takes up one electron to complete the octet, thereby forming a negatively charged system having the electronic arrangement of the inert gas, argon. Combination between sodium and chlorine can readily occur by the transfer of one electron from the sodium atom to the outer shell of the chlorine atom. By the loss of an electron the sodium atom acquires a positive charge, and by the gain of an electron, the chlorine atom acquires a negative charge ; and union takes place by electrostatic attraction. In this reaction, the sodium and chlorine atoms act as univalent atoms, the sodium, however, being electropositive and the chlorine electronegative. Similarly, calcium which has two electrons in its outermost shell, can give up these electrons and so act with a valency of two ; oxygen with six electrons in its outermost shell can take up two electrons to complete the octet, and it also is bivalent. Nitrogen with five electrons in the outermost shell can take up three more, and so exhibit a valency of three ; and so on. The valency which is thus manifested by the transfer of electrons, is known as *electrovalency*.

Chemical combination, however, may also take place by the *sharing* of electrons by atoms (*co-valency*), and in some cases, there may be a manifestation of both electrovalency and of co-valency. In such cases, atoms show a variable valency. The full consequences of this electronic theory of valency have still

to be worked out, and the brief survey which has been given must suffice.

**Transmutation and Sub-atomic Energy.**—Modern views regarding the constitution of matter and the discovery, more especially, of the phenomena of radioactivity, place in a new light the question of the transmutation of the elements, the achievement of which was one of the great aims of the mediæval alchemist.

Whether the elements such as we know them at the present day represent the halting points in a process of disintegration of more complex elements, or of integration from simpler units of matter, they appear to consist, for the most part, of stable atomic systems. In the case of the radioactive elements, however, we have atomic systems which pass into a condition of instability in which the nucleus of the atom undergoes a process of disintegration with the production of simpler atomic structures. In this way, a transmutation, not of lead to gold but of radium or of thorium to lead, takes place. The process of transmutation is spontaneous, and is not only a very slow one but is quite uncontrollable by man.

During radioactive transformations, great stores of energy existing in the atomic nucleus are set free. This sub-atomic energy is enormous compared with the energy liberated in even the most intense chemical reaction. It has been calculated, for example, that one pound of radon would, during its brief life of a few months, give out an amount of energy equal to that of an engine working at 128,000 h.p. for one day, or an amount of energy which is many million times greater than that given by an equal weight of the most powerful explosive known.

The discovery that large amounts of energy are liberated by the disintegration of radioactive substances, stirred the imagination and gave rise to the belief that in the complex atomic systems, the structure of which has been discussed in the preceding pages, there must exist inconceivably great, untapped and formerly unsuspected reservoirs of energy, compared with which the energy of combustion of all our fuel reserves is quite trifling. If one could only gain control of all the sub-atomic energy, or could control the process of atomic disintegration so as to bring it about at will, then, it was thought, untold stores of energy would be available to carry on the work of the world when the reserves of coal should be exhausted; or which, in the hands of the evilly-disposed, would suffice to shatter the globe. Neither this hope nor this fear, however, appears to be well-founded. For, apart from the few which are radioactive and which undergo spontaneous, uncontrollable disintegration, the

great majority of the elements are in a state of maximum stability, and are incapable of undergoing disintegration with liberation of energy. In fact, in order to break down the atoms of these elements, large amounts of energy must be expended on them.

The disintegration of elements was first experimentally realised in 1919 by Sir Ernest Rutherford, who found that when the atoms of nitrogen are bombarded by alpha particles, some of these particles, which are projectiles of great kinetic energy, registered direct "hits" against the nucleus of the nitrogen atoms and broke these up into hydrogen and helium. A few of the other elements have been similarly "transmuted." Although the amount of matter transmuted was infinitesimally small, yet the results so obtained are of great scientific interest as being the first cases of controlled transmutation of the elements. Dalton's aphorism: "Thou knowest no man can split an atom," has now lost its point.

Attempts to bring about a transmutation of elements, not by a disintegration of the nucleus but by introducing an electron into the nucleus, have also been made; and the claim has been put forward by several investigators that such a transmutation has been effected. Thus, it has been claimed that mercury, with the atomic number 80, has been transmuted into gold, with the atomic number 79; and the transmutation of lead to mercury has also been claimed. Both these claims, however, have been shown to be founded on error. Whatever the future may bring forth, it may safely be predicted that should the transmutation of lead to gold ever be effected it will be so only by the expenditure of energy infinitely greater in value than the gold obtained.

## CHAPTER VII

### THE THREE STATES OF MATTER

MATTER, we are accustomed to say, exists in the three physical states, the *gaseous*, the *liquid* and the *solid* or (as we ought rather to call it) the *crystalline*. These different states of matter, as we know, can pass one into the other when the external conditions are altered. A crystalline solid, *e.g.* ice, passes, when heated, into a liquid, water; a liquid, when heated, passes into a gas or vapour; and the reverse changes take place on lowering the temperature. One can distinguish between these three states by the fact that a crystalline piece of matter has a definite volume and form, a liquid has a definite volume but not a definite form, and a gas has neither a definite volume nor a definite form.

#### THE GASEOUS STATE

The term *gas* was coined by JEAN BAPTISTE VAN HELMONT, a distinguished iatrochemist and alchemist who was born at Brussels in 1577, and died in 1644. The word was formed from, and may indeed be regarded as a phonetic transcription of, the Greek word *χάος* (*chaos*<sup>1</sup>), something "without form and void." In Dutch, the language at that time of Brussels, the letter *g* has a guttural sound, similar to that of the Greek letter *χ* (*chi*).

In his views regarding disease and the use of drugs, van Helmont was a follower of Paracelsus, and it may be that the words of the founder of iatrochemistry: "Air is nothing more than a chaos. What air is, that is chaos. The element air is named chaos," were the inspiration of van Helmont's happily coined expression. Before that time, gases and vapours, the formation of which in the processes of calcination and distillation must have been recognised by the early alchemists and chemical craftsmen, were called, generally, by the names "spirit" (Lat. *spiritus*) and "air."

Until 1669, when the English physician, JOHN MAYOW (1640–

<sup>1</sup> The *ch* is pronounced as in the Scottish and German *Loch*.

1679), recognised that there exist various gases other than atmospheric air, chemists had thought of the different gases as being air containing various impurities; and it was only after STEPHEN HALES (1677–1761), perpetual curate of Teddington, Middlesex, and famous for his work in plant physiology, had devised an apparatus for the collection of gases evolved in chemical reactions, that progress was made in the preparation and study of gaseous substances. In the apparatus devised by Hales, which is the forerunner of the modern pneumatic trough, a glass globe, filled with water, was suspended in an inverted position with its mouth below the surface of the water contained

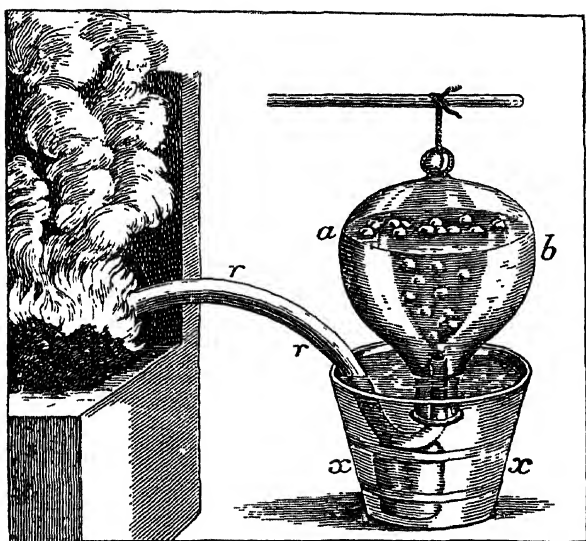


FIG. 12.—Hales' apparatus for collecting gases.

in a basin (Fig. 12). The tube conveying the gas from the retort or other apparatus opened under the mouth of the globe, and the gas, rising into the globe, displaced the water. By using mercury, Priestley was able, at a later time, to collect gases which are soluble in water.

**Diffusion.**—One of the most striking properties of a gas is that of filling uniformly any space that may be offered to it, no matter how large that space may be. In this respect a gas differs markedly from both liquids and solids. This property of *diffusion* makes itself evident, moreover, not only when a gas is allowed to diffuse into a vacuous space, but also when the space is already filled with another gas. This is really a very

familiar fact, for when the tap of a coal-gas burner is opened, or when some other evil-smelling gas, such as sulphuretted hydrogen, is allowed to escape, we know that in a comparatively short time the smell of the gas will be perceptible throughout even a large room. Whenever a vessel containing a gas is opened, the gas will escape and pass out of the vessel, like the Jinn from the brass bottle in the Arabian Nights.

Diffusion of a gas, moreover, can take place against the action of gravity, as a simple experiment will clearly demonstrate. If a glass bulb containing bromine be broken, by means of a rod, at the bottom of a closed cylinder containing hydrogen, it will soon be seen that the heavy brown vapour passes upwards to the top of the cylinder, although the bromine vapour is many times more dense than hydrogen.

The property of diffusion is one of much practical importance. Owing to diffusion, for example, marsh gas, escaping from the coal-measures, mixes with the air of the mine and produces the highly explosive "fire-damp," which has been the cause of many colliery disasters. On the other hand, diffusion assists ventilation and helps to keep fresh the air of rooms; and it prevents the dwellers in large cities, also, from being suffocated by the permanent accumulation of heavy poisonous gases which escape from the exhaust of motor cars or which are produced in various industrial processes.

Although the fact that diffusion takes place had been known for some time, it was not till 1829 that it was discovered by THOMAS GRAHAM (1805–1869)—who was, successively, Lecturer on Chemistry at the Andersonian Institution (now the Royal Technical College), Glasgow, Professor at University College, London, and Master of the Mint—that there is a connection between the rate at which diffusion takes place and the density of the gas; and, in 1833, as the result of special experiments which he carried out, Graham was able to enunciate the LAW OF DIFFUSION OF GASES. This law, generally known as Graham's law, states: *The velocity of diffusion of a gas is inversely proportional to the square root of the density.* The lower the density of a gas, the more rapidly does it diffuse.

Since the density of oxygen is 15.88 times as great as that of hydrogen, it is found, in accordance with Graham's law, that hydrogen diffuses more rapidly than oxygen in the ratio of  $\sqrt{15.88}$  to  $\sqrt{1}$ . That is, hydrogen diffuses very nearly four times as rapidly as oxygen. Similarly, since the density of atmospheric air is 14.4 times as great as that of hydrogen, the latter gas will diffuse 3.8 times as rapidly as air.

The fact that hydrogen diffuses with relatively greater velocity than air is clearly demonstrated by a simple and familiar experiment. The porous pot, A (Fig. 13), is connected by means of a glass tube with the bottle, B, which is filled with coloured water. At the commencement of the experiment, the porous pot and connecting tube are full of air. A beaker is then inverted over the porous pot, as shown in the illustration, and hydrogen gas is passed, by means of a tube, into the inverted beaker—hydrogen being much lighter than air. In a very few moments, owing to the fact that the hydrogen diffuses into the porous pot more rapidly than the air can diffuse out of it, the pressure inside the pot is increased and the water is forced out through the jet, C, in the form of a miniature fountain.

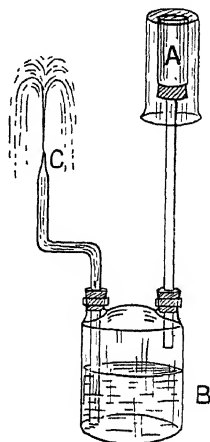


FIG. 13.—Diffusion.

**Boyle's Law.**—Repeatedly, in the history of science, it has happened that important advances or discoveries have been due, directly or indirectly, to the invention or perfection of some piece of apparatus; and it is to the invention of the air-pump by OTTO VON GUERICKE in 1650 that we owe the discovery by Boyle, ten years later, of the relation between the volume of a gas and the pressure to which it is subjected. Boyle was led to study this question by observing that when a partially inflated lamb's bladder was placed in the receiver of an air-pump, from which the air was then exhausted, the bladder became distended. The air appeared to possess, therefore, a certain elasticity or "spring," as Boyle called it, as if the particles, or molecules, composing it were little springs which could expand or contract according as the pressure on them was diminished or increased. In order to ascertain *quantitatively* how the expansion and contraction varied with the pressure, Boyle carried out what was really a very simple experiment. The bend of a glass tube, such as is shown in Fig. 14, was filled with mercury so as to enclose, in the shorter limb of the tube, a certain volume of air under the ordinary pressure of the atmosphere. This pressure, at the time of the experiment, was

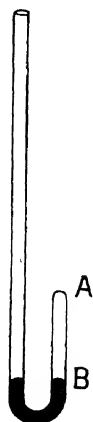


FIG. 14.—Boyle's tube.

found to be that of  $29\frac{1}{8}$  inches of mercury. The length of the space AB was measured, and mercury was then poured, in successive portions, into the open end of the tube. After each addition of mercury, the length of the air space and the difference of level of the two surfaces of mercury were determined. If the tube be of uniform bore, the volume of air in the closed limb of the tube will obviously be proportional to the length of the air column, and one can therefore ascertain how the volume of air varies with varying pressure, as measured by the difference of level of the mercury surfaces. Some of the values obtained by Boyle are given in the following table :

Length of air space in inches.	Difference in level of mercury surfaces.	Pressure in inches of mercury.
12	0	$29\frac{1}{8}$
10	$6\frac{3}{16}$	$6\frac{3}{16} + 29\frac{1}{8} = 35\frac{5}{16}$
9	$10\frac{3}{16}$	$10\frac{3}{16} + 29\frac{1}{8} = 39\frac{5}{16}$
8	$15\frac{1}{8}$	$15\frac{1}{8} + 29\frac{1}{8} = 44\frac{3}{8}$
7	$21\frac{3}{16}$	$21\frac{3}{16} + 29\frac{1}{8} = 50\frac{5}{16}$
6	$29\frac{1}{8}$	$29\frac{1}{8} + 29\frac{1}{8} = 58\frac{1}{4}$

From these numbers it is at once seen that the length of the air space is reduced from 12 to 6 inches when the pressure on the gas is increased from  $29\frac{1}{8}$  to  $58\frac{1}{4}$  inches of mercury ; that is, the volume is diminished to one-half when the pressure is doubled. In other words, the volume has varied inversely as the pressure. If this relationship holds in the other cases, then the values of the pressure multiplied by the corresponding values of the volume must give a constant number. Let us see if this is the case. We have,

$$\begin{aligned}
 12 \times 29\frac{1}{8} &= 349\frac{1}{2} \\
 10 \times 35\frac{5}{16} &= 353\frac{5}{8} \\
 9 \times 39\frac{5}{16} &= 353\frac{1}{8} \\
 8 \times 44\frac{3}{8} &= 353\frac{1}{2} \\
 7 \times 50\frac{5}{16} &= 352\frac{1}{4} \\
 6 \times 58\frac{1}{4} &= 352\frac{3}{4}
 \end{aligned}$$

As we see, the products are constant, with slight deviations which may be attributed to experimental errors.

Boyle also found that when the pressure was reduced, the volume increased, and he was thus able to sum up the behaviour of a gas in the general law : *When the temperature is kept constant, the volume of a given mass of gas is inversely proportional to the pressure ; or the product of pressure and volume is constant.* This is known as **BOYLE'S LAW**, and may be expressed algebraically in the form,  $p v = \text{constant}$ .

This inductively derived law was established by Boyle only



in the case of air and for comparatively small changes of pressure ; and it was not until after the first quarter of the nineteenth century that the behaviour of other gases was investigated. As a result of all the determinations which have been made, then and at more recent times, it has been found that Boyle's law holds for all gases, independently of the specific nature of the gas. It is a general property of gases. The law, however, is valid only for small changes of pressure ; and when the variations are greater, say, by several atmospheres or more, deviations from the law are found in all cases, and more especially in the case of those gases which can be easily liquefied. For most practical purposes, however, Boyle's law is sufficiently accurate.

**Gay-Lussac's Law.**—The volume of a gas varies not only with the pressure but also, and to a very marked extent, with the temperature. It is a familiar fact, and one which has been known for a very long time, that air expands on being heated. Even as far back as 100 B.C., the expansion of air on being heated was utilised by HERO of Alexandria for the automatic opening and closing of a Temple door, by means of the arrangement shown in Fig. 15. When a fire is kindled on the altar ADE, the air is caused to expand, and, passing through the communicating tube FG, forces water from the vessel H into the bucket XN, which is thereby caused to fall and, in doing so, rotates two pillars which cause the door to open. When the fire on the altar is extinguished, the air contracts and the water is drawn back from the bucket into the vessel H. A counterpoise causes the empty bucket to rise and also rotates the pillars so as to shut the door.

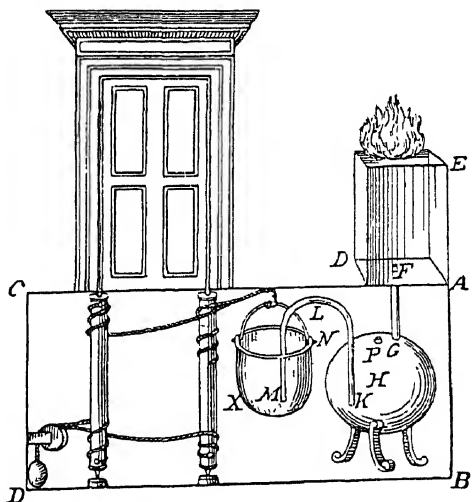


FIG. 15.—Hero's device for automatically opening a Temple door.

In 1787, the French physicist, JACQUES ALEXANDRE CHARLES (1746–1823), who was the first successfully to use hydrogen for filling balloons, found that oxygen, hydrogen, carbonic acid and air expand equally between 0° and 80° C., and the French chemist,

JOSEPH LOUIS GAY-LUSSAC<sup>1</sup> (1778-1850), in 1802, not only confirmed this but determined the amount of expansion which takes place. As a result of his measurements he was able to enunciate the law: When the pressure is kept constant, all gases expand or contract by  $\frac{1}{273}$  of their volume at 0° for each rise or fall of 1° C. If this law were valid to indefinitely low temperatures, the volume of a gas would become zero at -273° C. This is, of course, fictitious, as all gases pass into the liquid or solid state at temperatures above this, but it gives us the zero point of a new and, for many purposes, very useful scale of temperatures, known as the *absolute scale*. The temperature -273° C. is known as the absolute zero, and temperatures measured from this point are spoken of as absolute temperatures. The temperature on the absolute scale is therefore equal to the temperature on the centigrade scale plus 273; that is,  $t^{\circ} \text{C.} + 273 = T^{\circ} \text{A.}$

By adopting the absolute scale of temperature, the law of Gay-Lussac can be expressed in a much simpler form: *At constant pressure, the volume of a given mass of gas is proportional to the absolute temperature.*

Bearing in mind that the volume of a gas is inversely proportional to the pressure, and that the volume is directly proportional to the absolute temperature, Boyle's law and Gay-Lussac's law can be combined in the simple algebraic expression

$$pv = \text{constant} \times T,$$

or  $\frac{pv}{T} = \text{constant}$ , where T represents the temperature on the absolute scale. This expression is a succinct statement of the law that in the case of any given mass of gas, the product of the pressure and volume of the gas divided by the absolute temperature gives a constant value no matter what the particular values of the pressure, volume and temperature may be.

It will be clear that if a gas is enclosed in a vessel so that it cannot expand, then on raising the temperature the pressure must increase; and the algebraic expression which has just been given shows that, under these conditions, the increase of pressure is proportional to the absolute temperature.

The following example, relating to a matter of everyday interest, will illustrate the application of this law. At night, when the temperature is, say, 50° F., a motor-car tyre is inflated

<sup>1</sup> Of Gay-Lussac, who, from 1809 onwards, was Professor of Chemistry at the École Polytechnique and Professor of Physics at the Sorbonne, Paris, Sir Humphry Davy wrote in 1813: "Gay-Lussac was quick, lively, ingenious and profound, with great activity of mind, and great facility of manipulation. I should place him at the head of the living chemists of France."

to a pressure of 30 lbs. per square inch. During the day, the temperature rises to  $80^{\circ}\text{F}$ . What will then be the tyre pressure? Converting the temperatures on the Fahrenheit scale,<sup>1</sup> we have  $50^{\circ}\text{F} = 10^{\circ}\text{C} = 283^{\circ}\text{A.}$ , and  $80^{\circ}\text{F} = 26.7^{\circ}\text{C} = 299.7^{\circ}\text{A.}$  Since the pressure at  $283^{\circ}\text{A.} = 30\text{ lbs.}$ , the pressure at  $299.7^{\circ}\text{A.}$  will be  $\frac{30 \times 299.7}{283} = 31.8\text{ lbs.}$

**Normal Temperature and Pressure.**—Since the volume of a gas varies both with temperature and pressure, it will be clear that the volume of a given mass of gas will have a definite value only when the pressure and temperature are defined or specified. To render the comparison of gas volumes more easy, it is customary to reduce all volumes to standard or normal conditions of temperature and pressure, and as such one takes  $0^{\circ}\text{C}$ . (or  $273^{\circ}\text{A.}$ ), and the pressure of 1 atmosphere, which is assumed to be equal to the pressure of a column of mercury 76 cm. in height. These standard conditions are represented by N.T.P. (normal temperature and pressure).

The calculation of the volume of a gas at N.T.P. from the volume measured under other conditions, will be illustrated by the following example :

A given mass of gas occupies a volume of 250 c.c. at  $16^{\circ}\text{C}$ . and under a pressure of 77 cm. of mercury. What would the volume be at N.T.P.?

Since the volume is directly proportional to the absolute temperature and inversely proportional to the pressure, the volume at N.T.P. will be

$$\frac{250 \times 273 \times 77}{289 \times 76} = 239.3\text{ c.c.}$$

**Kinetic Theory of Gases.**—Can these laws of the behaviour of gases which have just been discussed, be related in any way to the general constitution of gaseous matter? What general conception, what hypothesis can be formed regarding the nature of a gas, such that the laws of diffusion, of Boyle, etc., will follow as natural consequences?

At one time the hypothesis was made that the particles of a gas repel one another, and one sought by means of this hypothesis to “explain” or account for the phenomenon of the diffusion of gases. On the basis of this hypothesis, however, it was not found possible to deduce, as a natural consequence, the quantitative behaviour of a gas. Last century, another hypothesis, which had first been suggested in 1738 by DANIEL

<sup>1</sup> See Appendix.

BERNOULLI (1700–1782), of Basle, and at various later times also by others, was worked out more especially by the German physicist, RUDOLF CLAUSIUS (1822–1888), in 1857, and by the English physicist, JAMES CLERK MAXWELL (1831–1879), in 1860. According to this hypothesis, matter in the gaseous state is composed of particles—the molecules of Avogadro—and these particles or molecules are assumed to be in rapid movement, darting about in straight lines with the speed of something like a mile per second, colliding ever and anon—some eighteen thousand million times a second—with other molecules, and pursuing, therefore, as a result of these collisions, a very zigzag course. It is by virtue of this motion which, according to the hypothesis, is inherent in the molecules, that a gas can distribute itself or diffuse rapidly throughout all the space which may be offered to it. That diffusion does not take place more rapidly than is actually the case, considering the very great velocity with which the molecules move, is of course due to the fact that the molecules are in constant mutual collision.

Moreover, the molecules, in their flight, strike against the walls of the containing vessel, and it is the bombardment of the walls of the vessel by the rapidly moving molecules of the gas, that constitutes the pressure of the gas.

The kinetic hypothesis, further, assumes that the increase of pressure of a gas with rise of temperature (the volume being kept constant) is due to an increase in the velocity of straight-line motion of the molecules, or to an increase in their kinetic energy.<sup>1</sup>

Such is the kinetic hypothesis of the constitution of a gas, and it was shown by Clausius and by Clerk Maxwell how this hypothesis could be developed mathematically into a *theory* which accounts not only qualitatively but also quantitatively for the behaviour of a gas. On the basis of this theory, one can deduce not only the law of diffusion, but also Boyle's law and the other laws of gases.

It is of interest, also, to note that the kinetic theory enables one to define the concept of temperature, by associating temperature with the kinetic energy of the molecules. According to the kinetic theory, the temperature of a system corresponds with a certain value of the mean kinetic energy of the molecules; and two bodies have the same temperature when the mean kinetic energy of their molecules is the same.

**Molecular Theory.**—Since, in the case of the kinetic theory,

<sup>1</sup> The kinetic energy of a particle is given by the expression  $\frac{1}{2}mv^2$ , where  $m$  is the mass of the particle and  $v$  the velocity of motion.

it is with molecules and not with atoms that we are concerned, it is of interest to enquire how the theory of molecules arose.

For the purpose of determining the composition of atmospheric air, a method had been introduced by the Italian physicist VOLTA, whereby a definite volume of air was mixed with hydrogen and the mixture exploded by means of an electric spark. Since by this means the oxygen of the air was removed by combination with hydrogen, the success of the method depended on a knowledge of the proportions by volume in which the hydrogen and oxygen combine. This ratio was determined in 1805 by GAY-LUSSAC, in collaboration with the German scientist and explorer, ALEXANDER VON HUMBOLDT (1769-1859), who was at that time resident in Paris; and it was found that two volumes of hydrogen combine with one volume of oxygen to form water. Impressed by the simplicity of the relative proportions thus found, Gay-Lussac extended his investigations to other gases, and in 1808 he was able to summarise his results in the form of a law, now known as GAY-LUSSAC'S LAW OF COMBINATION OF GASES BY VOLUME, which may be stated in the words: *Gases combine with one another by volume in the ratio of whole numbers, and generally small whole numbers; and the volume of the product, if gaseous, bears a simple ratio to the volumes of the reacting gases.* The volumes of the different gases must, of course, be measured under the same conditions of temperature and pressure.

In illustration of the above law, we give the following cases :

- 2 volumes of hydrogen combine with 1 volume of oxygen  
to give 2 volumes of water vapour.
- 1 volume of hydrogen combines with 1 volume of chlorine  
to give 2 volumes of hydrogen chloride.
- 1 volume of nitrogen combines with 3 volumes of hydrogen  
to give 2 volumes of ammonia.

The atomic theory of Dalton, we have seen, was introduced for the purpose of explaining the laws of combination by weight, and since it serves this purpose satisfactorily, it was only natural to attempt to employ it also as a basis for the explanation of the law of combination of gases by volume. According to the atomic theory, elements unite in atomic proportions which are represented by whole numbers—often small whole numbers; and since, according to Gay-Lussac's law, gaseous elements combine in simple ratios by volume, it seemed clear that there must be some simple relation between the number of atoms in equal volumes of reacting gases. What then is that relation?

The simplest hypothesis which suggested itself is that equal

volumes of gases (under the same conditions of temperature and pressure) contain the same number of atoms, the term atom being employed for the smallest particle of an element or of a compound. If this suggestion is tested, however, it is at once found to be unsatisfactory. For, let it be supposed that in a certain volume which we shall call unit volume, there are  $n$  atoms, then in the case of the combination of hydrogen and chlorine to form hydrogen chloride, we should have :

1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride.  
 $n$  atoms of hydrogen +  $n$  atoms of chlorine give  $2n$  atoms of hydrogen chloride,  
 or, 1 atom of hydrogen + 1 atom of chlorine give 2 atoms of hydrogen chloride.

Each "atom" of hydrogen chloride, however, must contain at least one atom of hydrogen and one atom of chlorine, and we should therefore have to assume that the original atom of hydrogen and of chlorine must have split into two. From the point of view of the atomic theory, this is, of course, the *reductio ad absurdum*.

The difficulty thus encountered was a serious one, but in 1811 it was surmounted by the Italian physicist, AMEDEO AVOGADRO (1776-1856), who was, like Dalton, a schoolmaster, and was, at a later time, honoured by being called to fill the Chair of Physics specially established for him in the University of his native town, Turin. Avogadro drew a distinction between *atoms*, or the smallest particles of an element which can take part in a chemical reaction, and *molecules*,<sup>1</sup> or the smallest particle of a substance, element or compound, which can exist free in a gas, or, as is generally said, which can exist in the free state. Even in the case of elements, Avogadro assumed, these molecules or free particles may consist, not of single atoms but of groups of like atoms; and he pointed out that a simple connection could be obtained between the laws of combination by weight and by volume if it is postulated that *equal volumes of all gases (elementary or compound), when under the same conditions of temperature and pressure, contain the same number of molecules*.

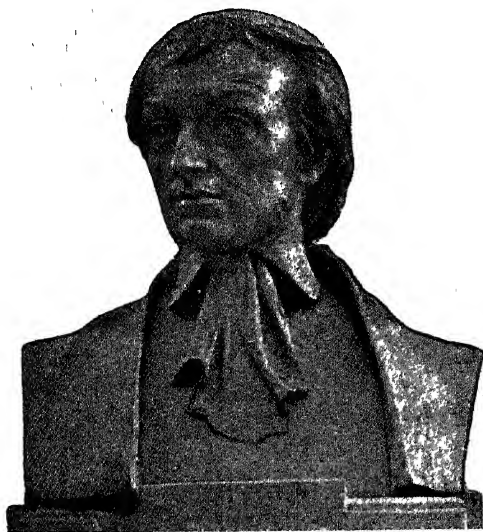
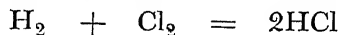
Adopting the hypothesis of Avogadro, we can say :

$n$  molecules of hydrogen +  $n$  molecules of chlorine give  $2n$  molecules of hydrogen chloride,  
 or, 1 molecule of hydrogen + 1 molecule of chlorine give 2 molecules of hydrogen chloride.

<sup>1</sup> Diminutive of Latin *moles*, a large mass.

If it be now assumed that each molecule of hydrogen and of chlorine contains two atoms, conflict with the atomic theory is avoided, for we can then say :

1 molecule containing 2 atoms of hydrogen combines with  
1 molecule containing 2 atoms of chlorine to give 2  
molecules of hydrogen chloride, each of which contains  
1 atom of hydrogen and 1 atom of chlorine ; or, using  
symbols and formulæ, we can write :



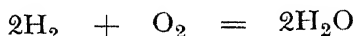
AMEDEO AVOGADRO.

From a sculpture by Pietro Canonica.

The assumption which has just been made, that the molecule of hydrogen and of chlorine each consists of two atoms, is the simplest assumption that can be made. Since it is also sufficient to account for, or explain, the facts, it is accepted as true. No other facts, moreover, are known which are not in harmony with this assumption.

Similarly, assuming the molecule of oxygen to consist of two atoms, we can write :

2 volumes of hydrogen + 1 volume of oxygen give 2 volumes  
of water vapour,  
or, 2 molecules of hydrogen + 1 molecule of oxygen give 2  
molecules of water vapour,  
or, in symbols,



Although in the case of the three gases hydrogen, oxygen and chlorine, the assumption that the molecule consists of two atoms has proved satisfactory, other cases are known in which one must conclude that the molecule consists of only one atom (*e.g.* helium, argon, etc.), or of three or of four atoms.

The hypothesis of Avogadro rounded off and completed the atomic theory of Dalton, and made it possible to surmount the difficulties of reconciling the laws of combination by weight and by volume. And it did more; it made it possible for the atomic theory to survive and to become of value in chemistry. The molecule became, as we shall learn later, the basis of reference for the atom, and the molecular weight a means of defining the atomic weight. Although the molecular hypothesis is, therefore, of fundamental importance in chemistry, this importance was not recognised by contemporary chemists. The molecular theory met not so much with opposition as with neglect; it was not rejected, it was ignored. And the reason is not far to seek. Like many another hypothesis, the hypothesis of Avogadro was born somewhat out of time, before knowledge was sufficiently advanced to give it confirmation or fully to realise its applications. For a theory, in order to be accepted, must find adequate experimental support and must not only explain the special law or phenomenon for which it is invented, but must show itself capable of wider application and of predicting new and independent laws and phenomena. And so it happened that it was not till 1858, by which time an adequate experimental basis had been laid by the organic chemists, that the value of the Avogadro hypothesis was made clear through its exposition and advocacy by Avogadro's fellow-countryman, STANISLAO CANNIZZARO (1826-1910), at that time Professor of Chemistry in the University of Genoa. Since then, the molecular hypothesis of Avogadro has been recognised as the corner-stone of chemical science.

**Gas Density and Molecular Weight.**—The importance of Avogadro's hypothesis depends not only on the reconciliation of the laws of combination by weight and by volume, but also on the fact that it points the way to a method of determining the relative molecular weights of gaseous substances. The relative weights of a given volume of different gases, at



the same temperature and pressure (generally at N.T.P.), represent the relative densities of the gases; and since, in the given volume, there are, according to the hypothesis of Avogadro, the same number of molecules of the different gases, the weights of the molecules must be proportional to the densities of the gases, or to the weights of equal volumes. This will be clearer, perhaps, if stated in the following equational form:

$$\begin{aligned} \frac{\text{Density of gas A}}{\text{Density of gas B}} &= \frac{\text{weight of a definite volume of A}}{\text{weight of the same volume of B}} \\ &= \frac{\text{weight of } n \text{ molecules of A}}{\text{weight of } n \text{ molecules of B}} \\ &= \frac{\text{weight of 1 molecule of A}}{\text{weight of 1 molecule of B}} \end{aligned}$$

Thus, the weights of one litre of hydrogen and of oxygen, at normal temperature and pressure, are 0.08987 gram and 1.42900 gram respectively. If the density of hydrogen is put equal to unity the density of oxygen is 15.90; or if oxygen be taken as the standard and its density put equal to the whole number 16.00, the density of hydrogen is represented by 1.007.<sup>1</sup> The molecular weights of oxygen and hydrogen must therefore be in the ratio of 16.00 : 1.007.

It has, however, been pointed out that it is necessary to assume that the molecule of oxygen consists of two atoms, and, therefore, if the atomic weight of oxygen is taken as 16.00, its molecular weight, or the weight of the molecule relative to the weight of the standard atom taken as 16.00, must be 32.00. Consequently, the molecular weight of hydrogen must be 2.014. Since this number is equal to twice the atomic weight, it must be concluded that the molecule of hydrogen also consists of two atoms.

On the basis of the hypothesis or postulate of Avogadro, the argument can be generalised and we can say: *The molecular weight of a substance, elementary or compound, in the gaseous state is numerically equal to twice the density of the gas, when the density is expressed relatively to the density of oxygen equal to 16.00.*

This extension of the hypothesis of Avogadro is one of extraordinary importance, its importance being enhanced by the fact that it can be applied to the determination of molecular weights not only of substances which are gases under normal conditions of temperature and pressure, but also of volatile

<sup>1</sup> The slight deviation of this value from that usually taken as the atomic weight of hydrogen (namely, 1.008) need not concern us here.

liquids and solids which can be converted by heat into gases or vapours. It was, indeed, the recognition of the value of Avogadro's hypothesis as an instrument for the determination of the molecular weight of volatile organic compounds, or compounds of carbon, that first led to an appreciation of its importance in chemistry.

**General Gas Equation.**—In discussing the influence of pressure and temperature on the volume of a given mass of gas, it was found that Boyle's law and Gay-Lussac's law could be united in the mathematical expression,  $\frac{pv}{T} = \text{constant}$ ; the value of the constant depending, of course, on the mass of gas and the nature of the gas considered. On the basis of the hypothesis of Avogadro, however, this equation can be generalised so as to give a constant of definite value in the case of all gases.

In the discussion of the application of Avogadro's hypothesis to the determination of molecular weights, it was learned that the weights of equal volumes of oxygen and hydrogen are in the ratio of 32.00 to 2.014; that is, in the ratio of their molecular weights. It follows, therefore, that 32.00 grams of oxygen occupy the same volume (under the same conditions) as 2.014 grams of hydrogen; or, generalising, the volume occupied by the molecular weight of any gas, expressed in the same unit of weight, is the same for all gases. If, therefore, we know the volume occupied by the molecular weight of oxygen expressed, say, in grams (the so-called *gram-molecular weight*), we shall also know the volume occupied by a gram-molecular weight of any other gas under the same conditions of temperature and pressure. Since 1 litre (1000 c.c.) of oxygen, at N.T.P., weighs 1.42900 gram, the volume occupied by one gram-molecule of oxygen (32.00 grams) will be  $\frac{1 \times 32}{1.42900} = 22.4$  litres. *One gram-molecule of any and every gas, therefore, will occupy a volume of 22.4 litres at N.T.P., a volume represented by a cube the length, breadth and height of which is 28.2 cm.*

The law which has just been stated makes the calculation of the molecular weight of a substance in the state of gas or vapour a very simple matter; for all that is necessary is to determine the weight in grams of a given volume of the gas or vapour at a known temperature and under a known pressure. The volume of this mass of gas at N.T.P. can then be calculated by means of the laws of Boyle and Gay-Lussac, and one can then calculate the weight in grams of 22.4 litres of the gas at N.T.P.

The number so obtained represents the molecular weight of the substance.

For example. A globe having a capacity of 116.6 c.c. was filled with a gas (carbon dioxide) at a temperature of 15° C., and under a pressure of 77 cm. of mercury; and the weight of the gas was found to be 0.220 gram.

Applying the laws of Boyle and Gay-Lussac, one finds the volume of the gas at N.T.P. to be

$$\frac{116.6 \times 273 \times 77}{288 \times 76} = 112.0 \text{ c.c.}$$

Since the weight of 112.0 c.c. of the gas at N.T.P. is 0.220 gram, the weight of 22,400 c.c. of the gas would be 44.0 grams. The molecular weight of the gas is therefore 44.0.

From what has been said, it will be clear that for a gram-molecule of any gas, at N.T.P., the values of  $p$ ,  $v$  and  $T$  must be the same; and consequently, the expression  $\frac{pv}{T}$  must have a constant value for all gases, irrespective of the nature of the gas. Since this constant value is generally represented by  $R$ , we obtain what is known as the general gas equation,  $p v = R T$ ; an expression which is valid for 1 gram-molecule of every gas. This expression is one which is of the greatest importance in chemistry.

**The Objective Reality of Molecules.**—The man of science, as we learned in the opening chapter, in his quest of truth, endeavours not merely to collect and order the data of observation or experiment concerning the material universe, but seeks also, by the divine gift of an intuitive intelligence, “to explain the complications of the visible in terms of invisible simplicity.” It was to such intuitive intelligence that we owe the atomic theory of Dalton, and its amplification and extension by Avogadro.

However much the Empedoclean conception of the continuity of matter appealed to the older thinkers, it has, in modern times, come to be recognised that “the notion of continuity is the result of an arbitrary limitation of our attention to a part only of the data of experience.” The farther we extend our investigations, the more refined and powerful the instruments we employ, the more does the coarse-grainedness of matter become evident.

The success with which the laws of chemical combination by weight and by volume could be explained on the basis of the atomic and molecular hypotheses, made it possible to regard these hypotheses as representing the invisible simplicity behind the

complications of the visible ; but the questions could not fail to arise and demand an answer : Do these hypotheses represent actual fact ? Do molecules really exist ? The investigations and discoveries of the present century make it possible to answer these questions with confidence. The properties of gases, the phenomena accompanying the discharge of electricity through gases, and the behaviour of radioactive elements have all contributed towards establishing the molecular hypothesis in a position of unassailable strength, and have furnished a proof of the objective reality of molecules. One may recall, for example, the success with which Rutherford counted the molecules of helium given off by radium.

The kinetic hypothesis which, as we have learned, was introduced into science about the middle of last century, was developed into a theory by applying to the still hypothetical molecules the general laws of mechanics. Not only did this molecular-kinetic theory serve admirably to account for the quantitative behaviour of gases, but it became possible, by its means, to calculate, on the basis of experimental data of various kinds, not only the absolute mass of the molecules, but also their dimensions and velocity of movement, and the number of them in a given volume of a gas. An account of these calculations cannot be given here, but the extraordinarily close agreement which was found between the values derived from the different kinds of measurement cannot but excite our admiration. And yet, the theory cannot carry complete conviction, by reason of the number of assumptions which it involves.

**Brownian Movement.**—Even as early as 1827, however, the molecules had, all unknown to their observers, made their presence manifest by the effects which they produced. In that year, the Scottish botanist, ROBERT BROWN (1773–1858), while examining suspensions of pollen grains under the microscope, observed that the particles were never at rest, but were in rapid motion, vibrating, rotating, moving irregularly along a zigzag path, sinking, rising—perpetually in motion. In this so-called *Brownian movement*—observed long before by the French naturalist, Buffon, and the Italian, Spallanzani, who saw in it a manifestation of life—we see, not, it is true, the molecules themselves, but the effect of the incessant bombardment of the coarser, visible particles of the suspensions, by the molecules of the liquid.

Over a lengthened period of time, the number of blows which a suspended particle, visible to the naked eye, would receive from the molecules of the liquid in which it is suspended, would

be the same in the different directions. The suspended particle, therefore, would show no sign of motion. If, however, we imagine the period of time made sufficiently short, the number of impacts of the liquid molecules will no longer be equal in different directions, the impacts will no longer balance one another; and if the suspended particle is made small enough it will, at each blow, be caused to move, first in one direction and then in another, and all the faster the smaller the particle. It is this motion of a particle under the blows which are rained upon it by the molecules of the liquid, that constitutes the Brownian movement. The suspended particles reveal the invisible molecular motion just as the bobbing of a cork may make manifest the tiny ripples on the surface of a mass of water. In the Brownian movement, therefore, we see a magnified picture, as it were, of molecular motion; and if this is so, then the molecular magnitudes calculated from the observed behaviour of fine suspensions should be the same as those calculated according to the molecular-kinetic theory. This conclusion was tested with great accuracy and in different ways, by the French physicist, JEAN PERRIN, Professor of Physics at the Sorbonne in Paris, and was found to be correct.

One example must suffice. As a result of the combined action of gravity and of the kinetic energy of the molecules, the molecules in a column of gas are more crowded together at the bottom of the column than at the top, in accordance with the law that when the distances from the bottom increase in arithmetical progression the concentration of the molecules diminishes in geometrical progression. If the microscopic particles in Brownian movement behave like the invisible molecules of a gas, then they also ought to arrange themselves according to the same law. This Perrin found to be the case. Thus, at different, equally-spaced levels<sup>1</sup> of a fine suspension of gamboge in water (Fig. 16), the number of particles counted were 100, 116, 146, 170, 200. These numbers are in agreement with the geometrical series,  $100 \times 1.19^0 = 100$ ,  $100 \times 1.19^1 = 119$ ,  $100 \times 1.19^2 = 142$ ,  $100 \times 1.19^3 = 169$ ,  $100 \times 1.19^4 = 201$ . These particles in Brownian movement, therefore, behave exactly as the molecules of a gas would behave according to the molecular-kinetic theory. In a number of other ways also, Perrin showed, the particles of a fine suspension in Brownian movement behave in exact accordance with the laws which have been deduced for the invisible molecules; and one cannot hesitate to believe that in the Brownian movement we have made manifest to us some-

<sup>1</sup> The heights of the different layers, therefore, were in arithmetical progression.

thing of the extraordinary stir and commotion which is going on in that world of molecules—now no longer hypothetical—which is beyond the reach of our direct observation.

Whether the fundamental molecular magnitudes are calculated from the viscosity of gases, from the Brownian movement of fine, but visible, particles, from the phenomena of radioactivity, or from the blue colour of the sky—by which also the discontinuous structure of matter is made manifest—the same results are obtained; and the real existence of molecules is thereby established with a probability amounting to, or bordering on, a certainty.

**Molecular Magnitudes and Avogadro's Number.**—Not only have the investigations of the present century, more especially, furnished unmistakable evidence that matter is made up of molecules, but it is possible, on the basis of these investigations, to calculate the number and magnitude of these inconceivably minute particles with an accuracy which is altogether astounding; indeed, as the American physicist, R. A. Millikan, has pointed out, the molecules in a given mass of matter can be counted “with as much certainty and precision as we can attain in counting the inhabitants of a city.”

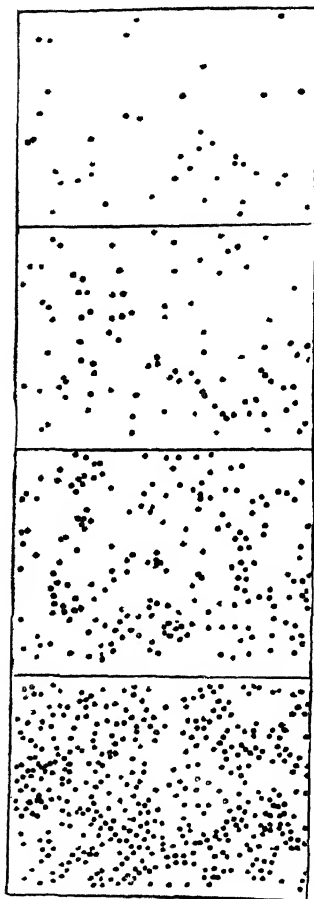


FIG. 16.—Distribution of small particles in a suspension.

Rutherford, as we have seen (p. 84), found, by a direct count, that there are  $27,500,000,000,000,000$ , or, as it is more conveniently expressed,  $2.75 \times 10^{19}$  molecules of helium in 1 c.c. of the gas at N.T.P.; and, therefore, in 22.4 litres, the volume occupied by 1 gram-molecule (p. 110), there will be  $2.75 \times 10^{19} \times 22,400 = 6.16 \times 10^{23}$  molecules. But Perrin, from his investigations of the Brownian movement of minute particles, calculated that the number of molecules in 1 gram-molecule is  $6.06 \times 10^{23}$ , and similar values have been derived from the consideration of very widely differing properties of many different substances.

As a result, it may be concluded that the number of individual molecules in 1 gram-molecule of a substance is  $6.06 \times 10^{23}$ , a number which is the same for every substance and which goes by the name of *Avogadro's number*.

A further interest attaches to these calculations. The volume occupied under given conditions of temperature and pressure by one gram-molecule of a gas is the same for all gases, and, therefore, since the number of individual molecules in one gram-molecule is the same for all substances, the number of individual molecules in a given volume of a gas must be the same for all gases. At N.T.P., 1 c.c. of any and every gas contains  $2.70 \times 10^{19}$  molecules. The postulate of Avogadro ceases to be a hypothesis; it becomes a law.

The numbers which we have just been considering greatly exceed our powers of comprehension. The molecules in a single dewdrop are so numerous that if they were distributed equally there would be a million million for each of the 1,500,000,000 inhabitants of the world; and if one of those inhabitants, suspicious of the equality of the distribution, started in to count the numbers in his allotment, it would take him thirty years, counting out bundles of a thousand molecules each second, night and day, to complete his task.

As regards the size of the molecules, these vary comparatively little, as the following numbers show:

	Diameter of molecule.
Helium . . . . .	$2.22 \times 10^{-8}$ cm.
Hydrogen . . . . .	$2.68 \times 10^{-8}$ cm.
Oxygen . . . . .	$3.62 \times 10^{-8}$ cm.
Water vapour . . . . .	$4.54 \times 10^{-8}$ cm.
Carbon dioxide . . . . .	$4.56 \times 10^{-8}$ cm.

The hydrogen molecule, we see, is rather less than  $1/300,000,000$ th of a centimetre in diameter, and the diameters of the other molecules are of the same order of magnitude. In the case of a gas under ordinary conditions the volume of the molecules is small compared with the total volume of the gas; or, the total volume is composed mainly of empty space. This explains why different gases obey Boyle's law.

Since the number of molecules in one gram-molecule of a substance is known, the mass of a single molecule can be calculated by dividing the molecular weight of the substance expressed in grams by the Avogadro number. Thus, the mass of a hydrogen molecule is  $\frac{2.016}{6.06 \times 10^{23}}$  gram, or  $3.3 \times 10^{-24}$  gram.

## CHAPTER VIII

### THE THREE STATES OF MATTER (*continued*)

#### THE LIQUID STATE

IN the gaseous state, the molecules of matter, as we have seen, are relatively far apart, and in perpetual, rapid motion. If the temperature is raised, the velocity with which the molecules fly about increases; if the temperature is lowered, the velocity diminishes. In the case of a gas, the rapid motion of the molecules is sufficient to overcome the attractive forces which exist between the molecules, so that the molecules lead an existence of complete, or practically complete, independence. As the temperature of a gas is lowered, the violence of molecular motion is subdued, and, at a certain temperature, the motion of the molecules, or rather, of some of them (for all do not move with the same velocity), is reduced to such an extent that the more sluggish molecules are no longer able to overcome the force of mutual attraction or cohesion; they become attached or cohere to one another and a liquid is obtained. This process of condensation or liquefaction will, of course, be helped by an increase of pressure (or diminution of the volume of the gas), as well as by reduction of temperature. In a liquid, the kinetic energy of the molecules is no longer sufficient to keep them entirely free as in the case of a gas, and they cling together to such an extent that the liquid has a definite volume. The molecules, however, are not rigidly attached to one another; they are still in motion, "like a shoal of fish in the sea," and there is a continual interchange of partners.

**Surface Tension.**—When a liquid is withdrawn from the action of gravity by suspension in a medium of the same density as itself, it assumes the shape of a sphere; and whenever a free surface is produced, the liquid tends to form the smallest possible surface—as in the case of the sphere. This behaviour is due to the mutual attractions of the molecules, and can be observed very clearly when olive oil is carefully run into a mixture of alcohol and water of the proper density, or when the liquid,



ortho-toluidine, is suspended in a solution of salt in water. The oil and the ortho-toluidine assume the spherical form.

The molecules in the interior of such a drop, it is clear, will be attracted equally in all directions by surrounding molecules, but the molecules in the surface layer are obviously subject to an unbalanced force of attraction acting inwards at right angles to the surface. This force is spoken of as the *surface tension*, and we can picture to ourselves the action of this force by imagining the surface layer of a liquid to act as an elastic skin which tends to contract uniformly.

The existence of a surface tension and the fact that the surface layer of a liquid acts as if it were an elastic skin, afford an explanation of a number of more or less familiar phenomena. If a little mercury be dropped on a table, it breaks up into drops. Under the action of gravity, the larger drops flatten out, but the smaller ones form almost perfect spheres. Similarly, if water is brushed over a piece of greasy paper or other surface which it does not wet, it does not spread evenly as a film, but forms into drops owing to the action of surface tension. If, however, the surface tension is reduced—that is, if the imaginary surface skin is weakened—the water will spread out as a film over the paper. The lowering of the surface tension can be brought about by the addition of various substances; ox-gall, for example, may be used, as in the case of water colours. It is, moreover, owing to the existence of a special layer that it is possible to float a steel needle or a boat of wire gauze on the surface of water. So long as the needle or wire gauze is not wetted by the water, it will merely form a depression or series of depressions on the surface of the liquid, as if resting on a thin elastic film (Fig. 17). If, however, the surface tension of the water is lowered by the addition of soap, ox-gall or some other substance, the needle or gauze breaks through the surface layer and sinks.



FIG. 17.—Wire gauze floating on the surface of water.

Edward Lear, in his *Nonsense Verses*, tells us how

They went to sea in a sieve, they did,  
In a sieve they went to sea;  
In spite of all their friends could say,  
On a winter's morn, on a stormy day,  
In a sieve they went to sea;

and, long before Lear, Shakespeare makes one of the witches in *Macbeth* declare,

And in a sieve I'll thither sail.

Now we can understand how the studied nonsense of the poet becomes the commonplace of science, and how a feat which in popular judgment was deemed impossible, is susceptible of a simple explanation.

And just as one can float a sieve on water, so one can carry water in a sieve, a fact which, doubtless, was known in ancient times, for we are told that the carrying of water in a sieve was one of the trials by ordeal to which a Vestal virgin, accused of breaking her vows, was subjected.<sup>1</sup>

In the destruction of the larvæ of mosquitoes, the carriers of malaria, by pouring oil on the surface of the breeding pools, we have an operation of great economic importance in which surface tension plays a part. Normally, the larvæ can remain suspended by their unwetted breathing tubes from the surface of the water; but when oil is poured on the water the surface tension is lowered and the larvæ sink and are drowned.

Owing to the existence of a surface tension, a liquid ascends in a capillary tube, provided it wets the tube; and water rises in a strip of blotting paper or ascends in the soil, in the latter case often to a height of several feet.

**Vapour Pressure.**—Although the molecules of a liquid, as a whole, are unable to overcome the force of cohesion, yet the molecules are not all moving with the same velocity, and it may happen that some, having a higher velocity than the average, are able to tear themselves away from the general mass and escape into space, where they move about freely as the molecules of a gas (or vapour). The liquid evaporates.

Since the molecules which break away from the surface of a liquid and pass into free gas molecules are those which possess a relatively large amount of energy, the average kinetic energy of the remaining molecules will decrease; that is, the temperature (which is measured by the kinetic energy) falls. A liquid becomes colder through evaporation, as any one may observe by wetting the hand and blowing on it; and the cooling effect produced by the evaporation of perspiration is one of Nature's most effective means of regulating the temperature of the body. In hot and dry countries, also, water is kept cool by placing it in porous earthenware vessels or canvas bags. Water slowly soaks through the porous ware or canvas and evaporates from the outer surface,

As is related of the Vestal virgin Tutia, who procured her acquittal when accused of having broken her vows: "Having seized a sieve, she prayed: 'Oh, Vesta, if always with chaste hands I have touched thy holy mysteries, grant that I may draw water in this sieve from the Tiber and carry it into thy temple.' When, boldly and daringly, she had made her votive offerings to the priest, the very nature of things yielded to her wishes."—*Valerius Maximus*.

especially if the vessel be placed in a current of air, and the water which remains is thereby cooled. By the rapid evaporation of water, the temperature may be lowered to such an extent that the water freezes, and, from very early times, ice has been obtained by the natives of India by exposing water in shallow pans embedded in straw to prevent access of heat. On a cool clear night, evaporation takes place so rapidly that the water freezes.

If a liquid is placed in a closed vessel so that the escaping molecules cannot pass away into space, it is found that a pressure is produced by the molecules

which escape from the liquid, as can be shown by breaking a bulb of ether in a bottle fitted with a manometer or pressure gauge (Fig. 18). The pressure thus produced, however,

does not go on increasing indefinitely, but for each temperature there is a certain maxi-

mum value for a given liquid. At this point, as many molecules pass back into the liquid as escape from the liquid. There exists, therefore, an *equilibrium*.

As the temperature is raised, the equilibrium pressure which is produced, the so-called *vapour pressure*, increases (Fig. 19), and when the pressure of the vapour is equal to the external pressure, or pressure on the liquid, the liquid boils. The boiling-point of a liquid, therefore, is simply that temperature at which the equilibrium vapour pressure of the liquid is equal to the pressure on the liquid; or the temperature at which vapour mole-

cules are produced in such abundance that they are able to lift or push back the mass of air resting on the liquid. If we increase this external pressure, the boiling-point is raised; if

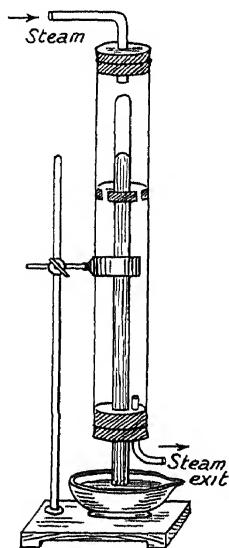


FIG. 19.—Increase of vapour pressure with temperature.

A small quantity of water is introduced into the vacuum of a barometer tube standing over mercury and surrounded by a wider jacket. Steam is passed through the jacket, the water in the barometer is heated, its vapour pressure increases and the mercury falls progressively.

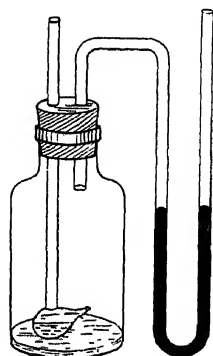


FIG. 18.—Vapour pressure of liquids.

When the bulb of ether is broken, the mercury in the left-hand limb of the U-tube is depressed.

we decrease it, the boiling-point is lowered. On the top of a mountain, water boils at a lower temperature than it does on the seashore; and for every 295 metres (about 960 feet) of ascent, the boiling-point of water falls  $1^{\circ}$  C.

When a liquid is boiling freely, its temperature remains constant no matter how much heat is added to the liquid; for the added heat is all used up merely for the purpose of overcoming the cohesive forces of the molecules and of converting the liquid into gas or vapour. The heat required to bring about a change of state from liquid to vapour, without producing an alteration of temperature, is called the *latent heat of vaporisation*. The discovery of latent heat we owe to the Scottish chemist, JOSEPH BLACK (1728–1799), while Professor of Chemistry in the University of Glasgow.

**Liquefaction of Gases.**—In order to bring about the liquefaction of a gas, it is necessary, as we have seen, to diminish the kinetic energy of the molecules by lowering the temperature of the gas, so that the molecules may cohere. The process is assisted by increase of pressure or diminution of volume. The conditions of temperature and pressure necessary to bring about liquefaction vary very greatly for the different gases, for while sulphur dioxide, the choking gas formed when sulphur is burned in air, can be liquefied under ordinary atmospheric pressure merely by cooling the gas to below  $-8^{\circ}$  C., carbon dioxide must be cooled to below  $-78.2^{\circ}$  C., and oxygen to below  $-182.5^{\circ}$  C. Since, however, pressure assists condensation, sulphur dioxide can be liquefied even at  $20^{\circ}$  C., if the pressure be increased to 3.24 atmospheres; and so we find liquid sulphur dioxide supplied commercially in strong glass “syphons,” from which gas or liquid can be drawn off as required.

Although the condensation of vapours to liquids was well known to the ancient workers who practised the art of distillation, it was not till towards the end of the eighteenth and beginning of the nineteenth century that the view was generally held that even those substances which are gases under ordinary conditions may also be reduced, by a lowering of temperature or an increase of pressure, to the liquid state. While the attempts of the earliest workers—among whom may be mentioned, more especially, THOMAS NORTHMORE (1766–1851), classical scholar and amateur of natural science, and MICHAEL FARADAY (1791–1867)—to liquefy gases were crowned by a large measure of success, a certain number of gases, such as hydrogen, oxygen, nitrogen and air, proved refractory. All attempts to obtain these substances in the liquid state having proved unsuccessful,

the gases were regarded as being uncondensable and were therefore spoken of as *permanent gases*. In 1869, however, the reason for the failure to liquefy the so-called permanent gases became clear through the work of THOMAS ANDREWS (1813–1885), Professor of Chemistry in Belfast.

On compressing carbon dioxide at the ordinary temperature (say,  $15^{\circ}\text{C.}$ ), the volume diminishes in accordance, more or less, with Boyle's law, until, at the pressure of about 50 atmospheres, liquefaction takes place. A similar behaviour is found at all temperatures below  $31.1^{\circ}\text{C.}$ , but above this temperature no liquid makes its appearance, no matter how greatly the pressure may be increased. For other gases, also, Andrews showed that there exists, in each case, a particular temperature, known as the *critical temperature*, such that below this point liquefaction can occur if the pressure is sufficiently high, but above this temperature liquefaction cannot occur, no matter how great the pressure may be. Since the critical temperatures of hydrogen, oxygen and nitrogen are  $-234.5^{\circ}$ ,  $-118^{\circ}$  and  $-146^{\circ}\text{C.}$ , respectively, the failures of the earlier experimenters to achieve the liquefaction of these gases were due to their inability to bring about a sufficient lowering of the temperature.

The change of a liquid to a gas at the critical temperature can be seen very clearly when ether, for example, is heated in a strong, sealed glass tube, from which the air has been removed (Fig. 20). As the temperature of the critical point is approached, the liquid meniscus becomes billowy and indistinct, and then suddenly disappears altogether when the critical temperature is reached.

It is clear, therefore, that the successful liquefaction of gases depends on the production of a sufficiently low temperature. For the production of low temperatures various means have been adopted, and of these the oldest and most familiar makes use of the *latent heat of fusion* of ice, or the heat which is required to convert ice to water at the same temperature. It was known to Boyle and the Florentine physicists of the seventeenth century, that when ice and salt are mixed together, the ice melts and the temperature falls; and the temperature so produced was thought by Fahrenheit to be the lowest temperature possible and was used by him, in 1724, to represent the zero of his thermometric scale

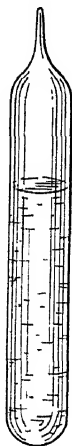


FIG. 20.—Critical temperature of ether.

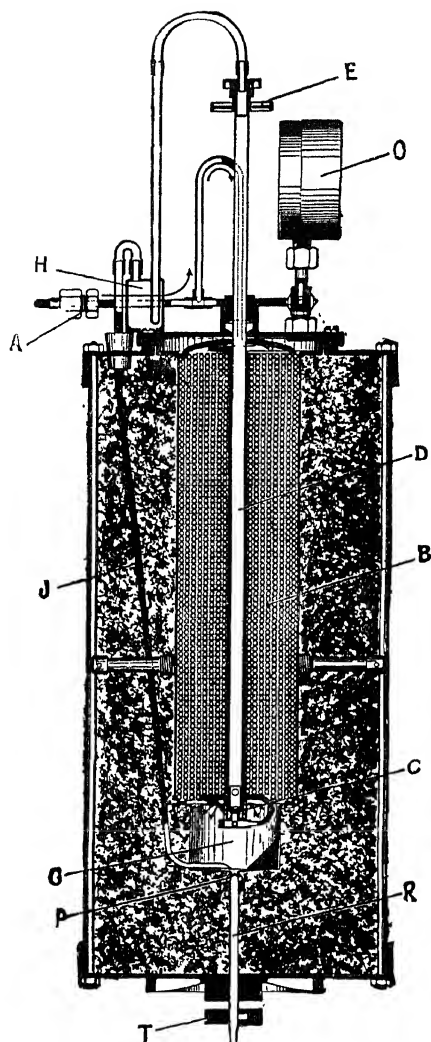


FIG. 21.—Hampson apparatus for liquefying air.

A, tube by which air enters; B, section through spirals of copper tubing; C, expansion valve; D, central spindle; E, wheel for opening and closing expansion valve; G, tank in which liquid air collects; H, gauge to indicate amount of liquid air in G; J, tube connecting tank with gauge; O, pressure gauge to indicate pressure at which the air enters the apparatus; P, valve closing tube R, through which the liquid air is withdrawn; T, wheel for opening the valve R.

( $0^{\circ}\text{F.} = -16.6^{\circ}\text{C.}$ ). By using 1 part of snow with 2 parts of crystalline calcium chloride, a temperature of  $-42^{\circ}\text{C.}$  can be obtained. One may, however, make use not of the latent heat of fusion of ice but of the latent heat of evaporation of a liquid, and by this means low temperatures can also be produced. The cold produced by the boiling of liquid ammonia, liquid sulphur dioxide and other liquids under reduced pressure is made use of for the commercial production of ice, and the method is also made use of in certain domestic refrigerators.

About 1896, however, another method of producing a lowering of temperature was introduced by means of which all the so-called permanent gases, even the most difficultly liquefiable gas helium, can be liquefied. The method depends on the fact that if a highly compressed gas is allowed to escape through a valve into a region of low pressure, heat is used up in overcoming the force of attraction or cohesion between the molecules, and this heat is taken up from the molecules themselves. The kinetic energy of the molecules is thereby diminished, or the temperature falls. The fall of temperature on expansion, moreover, is all the greater the lower the initial temperature of the compressed

gas. This principle was made use of by SIR JAMES DEWAR (1842–1923), of the Royal Institution, London, for the liquefaction of large quantities of air and of oxygen, and the industrial application of the principle is due mainly to a German and an English engineer, C. von LINDE and W. HAMPSON. The method employed will be understood from Fig. 21. Air, under a pressure of about 150 atmospheres and free from moisture and carbon dioxide, enters the apparatus at A, and passes through the spirally-wound tube, B, to a valve C. Here the compressed air expands into a closed space. The temperature of the air falls on expansion. The cool air now passes back over the tubes, B, and thereby lowers the temperature of the incoming compressed air. In this way the air expanding at the valve gets progressively colder and colder, until at last a point is reached when the fall of temperature on expansion is so great that the air liquefies. This liquid air collects in the tank G and can be run off from time to time through the tube R.

By the method just described, many millions of gallons of liquid air are now produced daily for use in industry. In the case of air, no preliminary cooling of the compressed gas below the ordinary temperature is necessary, but, in the case of hydrogen and of helium, the gas must first be cooled down to a low temperature by means of liquid air, before expansion takes place.

The ease with which liquid air can now be produced is not only of great industrial importance, but is also of much value in the furtherance of scientific knowledge. By means of liquid air, one is enabled to extend the scope of scientific investigation to temperatures which otherwise would be inaccessible and which, in the middle of last century, would have been regarded as unattainable; and the increase of knowledge which has accrued therefrom is of the highest scientific interest and practical value.

The utilisation of this new aid to scientific research was made possible, or, in any case, was greatly facilitated by the introduction of the well-known Dewar "vacuum vessels." These Dewar vessels, which are now so familiar under the name of "thermos" flasks, consist of double-walled glass vessels<sup>1</sup> (Fig. 22), the air being removed as completely as possible from the space between the two walls. The "vacuum" by which the vessel containing the liquid air is thus surrounded acts as a

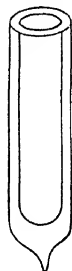


FIG. 22.—Dewar vacuum vessel.

<sup>1</sup> Dewar vessels made of metal are now also available.

very efficient heat insulator, because there are now no air molecules to conduct the heat from the outside to the liquid air. The transmission of heat by radiation is prevented by silvering the outer wall of the vessel. Although the temperature of liquid air is about  $190^{\circ}$  C. below that of the atmosphere, the liquid may be preserved for hours without any very great loss.

### THE CRYSTALLINE STATE

When one examines a perfectly formed crystal, one cannot but admire the regularity of outline and the smoothness and lustre of the crystal faces. The crystalline form, however, not only appeals to our sense of beauty and orderliness, but is also of very great practical importance, for the properties of solid matter depend largely on the nature and arrangement of the crystals of which it is composed. In metallurgy, to take only one example, the manufacture and tempering of steel, and the production of the numerous alloys now employed, depend largely on the production of suitable crystalline structures. It is, therefore, of importance to understand something of the laws of crystal growth, structure and behaviour.

When a substance is cooled down from the gaseous state, the movement of the molecules, we have learned, becomes more and more sluggish, until it is no longer able to overcome entirely the mutual attraction of the molecules. A liquid is then produced. As the temperature is lowered still farther, the forces of attraction between the molecules gain more and more the upper hand over the disrupting and separating action of the molecular motions; and, under favourable conditions, molecule joins itself to molecule, not vaguely and uncertainly in loose attachment, but in a firm linking together at definite points. Molecular motion still exists, but is restricted to a vibration or oscillation about certain fixed points. In this way, out of the general welter, small groups of molecules are formed in definite array. Around each such invisible group of molecules, other molecules marshal themselves, each taking up the position assigned to it by nature; and so, out of chaos, order begins to arise, and the structure grows into the visible crystal, the sign and symbol of "immortal Nature's ageless harmony."

**Melting-point and Freezing-point.**—The change of state from crystalline solid to liquid is associated with a perfectly definite temperature. Thus, under ordinary conditions, that is, under atmospheric pressure, ice melts at  $0^{\circ}$  C. At this temperature, in the case of ice, the molecular motions become



sufficiently violent to disrupt the molecular linkages of the crystal group. We might expect, therefore, that on cooling a liquid down to the melting-point of the crystalline solid, the liquid would begin to crystallise, but, in most cases, this does not occur. The molecules, so to speak, do not know how to arrange themselves into the stable crystalline grouping; there is nothing, as it were, to guide them to the places they should take up. One finds, therefore, that it is frequently or generally possible to cool a liquid down considerably below the temperature at which the solid melts, without any crystallisation taking place. The liquid is then said to be *supercooled*. In order that crystallisation shall take place, a "centre of growth" or a "nucleus" must first be formed, round which the other molecules may group themselves. In most cases, if the cooling is carried out sufficiently slowly, nuclei or stable crystal units are formed spontaneously, by the accidental meeting, it may be, of the molecules in a suitable way; and vigorous stirring assists these favourable encounters. In some cases, however, spontaneous formation of nuclei may not take place, and it may be necessary to introduce a small crystal from the outside in order to start the process of crystallisation. Thus, if a glass rod on the tip of which is a tiny crystal of sodium thiosulphate (photographer's "hypo."), is introduced into a flask of molten thiosulphate, crystallisation at once takes place, not throughout the whole mass of liquid, but starting from the crystal on the rod; and only those parts of the supercooled liquid which are in contact with the solid, crystallise out (Fig. 23). If the rod with its clump of crystals is removed, crystallisation stops.

**Velocity of Crystallisation.**—When crystallisation is started in a supercooled liquid, the process extends throughout the liquid, not instantaneously but with a certain finite speed or velocity, which depends not only on the nature and purity of the substance, but also on the degree of supercooling. The more a liquid is cooled below the normal freezing-point, or the greater the degree of supercooling, the faster will crystallisation take place, once it is started. But this law, although a quite general one, is subject to modification through the operation of another factor. As the temperature is lowered, the rate of motion of the molecules in the liquid becomes less, the cohesion between

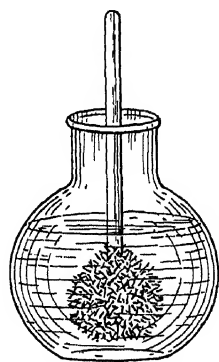


FIG. 23.—Growth of crystals.

them increases, and so the molecules cannot move so quickly to their places in the crystalline structure. At first, then, we find that as the degree of supercooling is increased, the velocity of crystallisation also increases, but after a point the increasing sluggishness of molecular movement makes its effect felt more and more. The rate of crystallisation then ceases to increase as the temperature of the supercooled liquid is lowered, and in fact begins to decrease. There is, therefore, a certain degree of supercooling at which the velocity of crystallisation is a maximum. Below this temperature, the velocity of crystallisation rapidly decreases and at last becomes practically equal to zero. The supercooled liquid now no longer crystallises even when brought into contact with the crystalline solid. It is in this way that glasses or *amorphous solids* are formed; a glass or amorphous solid being merely a liquid supercooled to such a degree that through increase of viscosity it does not "run" perceptibly, and the rate of crystallisation is practically zero.<sup>1</sup> From what has just been stated, it is easy to understand why the term "solid state" is not a sufficiently accurate or well-defined term, for an amorphous solid is to be regarded as a supercooled liquid. We ought, therefore, to speak rather of the crystalline state.

When a "glass" is maintained for some time at a temperature in the neighbourhood of the softening point, spontaneous crystallisation may set in, and the glass thereby loses its transparent, vitreous or glassy character. The glass is said to *devitrify*.

So far, we have spoken of crystallisation of a substance from the state of fusion. Crystallisation, however, may take place also from solution, as when salt crystallises from sea-water or from brine. In an ordinary solution, the molecules of the dissolved substance are kept apart by the molecules of the solvent, but as the solution is concentrated by evaporation of the solvent, the dissolved molecules become more crowded together; and when a certain concentration or crowding is reached, the molecules join up into crystal units, to which, as evaporation proceeds, more and more molecules attach themselves in orderly array.

Although, in the passage from the liquid to the crystalline state, nature is wont to marshal the molecules into the ordered harmony of the crystalline form, the production of a perfect crystal requires the exercise of great care and the existence of

<sup>1</sup> Recent investigation has shown that this view, though generally held, may have to be somewhat modified.

favourable conditions. For example, the growth of the crystal must be slow, in order that the molecules may have time to arrange themselves properly; and the crystal also must be allowed to grow freely in all directions. When these conditions do not exist, the crystal becomes distorted in various ways, and great deviation from the form of the perfect crystal may be observed. Thus, when a thin layer of liquid crystallises on a flat plate, growth can take place in practically only two dimensions, and flat fan-like or fern-like crystals are formed. This is

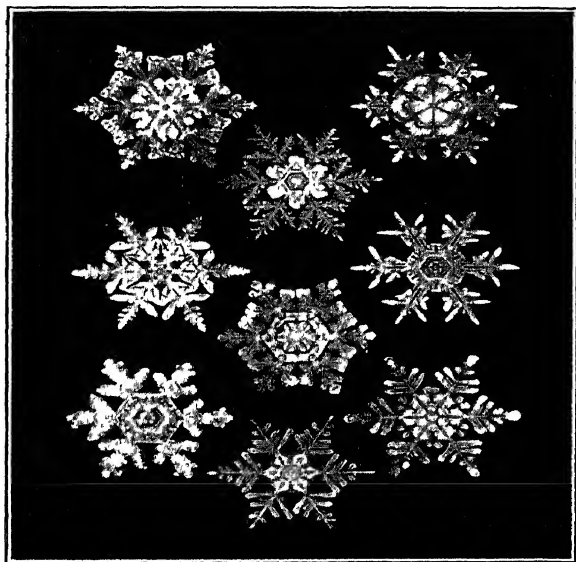


FIG. 24.—Snow crystals.

observed, for example, when moisture freezes on the window-pane. Such distorted crystals are called *dendrites*<sup>1</sup> or dendritic crystals, from their resemblance to tree growth. Beautiful examples of leaf-like and lace-like skeleton crystals, formed owing to crystalline growth being more rapid in certain directions than in others, are frequently seen in the case of snow-flakes (Fig. 24).

**Crystalline Structure.**—The comparatively large crystals which one can see and handle may be regarded as built up of a

<sup>1</sup> From the Greek *δένδρον* (*dendron*), a tree.

large number of crystal units, each unit having the same form as the large crystal. There is a repetition, therefore, throughout the whole crystal of a fundamental crystal unit or *crystal lattice*, as it is called. When, therefore, we pass from the consideration of the general laws of crystal formation and crystal growth and turn our attention to the internal structure of crystals, we are faced with the questions: What are the dimensions of the single crystal unit? How are the atoms or molecules arranged within it? How is the crystal lattice itself built up?

On first thought, it may seem hopeless to try to determine the position and arrangement of atoms which are much too small to be seen even with the aid of the most powerful microscope; yet the instruments of investigation which scientific genius and inventiveness have made available, render the task no longer impossible.

A large rock or cliff, against which the waves of the ocean break, can deflect and reflect the waves and so produce disturbances which make the existence of the rock or cliff manifest; but a small pebble is powerless to disturb appreciably the uniform roll of the waves, and so its presence cannot be detected. If, however, the waves dwindle to tiny ripples, then even a pebble may produce a detectible disturbance and so give evidence of its presence. Similarly, an object can be seen only when it is large enough to cast a shadow or reflect the light or interfere in some way with the waves of light. Although the waves of ordinary light are too large to be affected by the presence of atoms in any way which the eye can appreciate, X-rays are some ten thousand times smaller than the waves of ordinary light, and so, by means of X-rays, one is able to detect objects ten thousand times more minute than those which can be detected with ordinary light. By means of their action on X-rays, then, atoms and molecules may, as it were, be rendered visible, and thus the position and arrangement of the atoms or molecules which build up the crystal lattice have been determined.

When a beam of X-rays is thrown on the surface of a crystal, the successive layers of atoms, lying in planes parallel to the crystal face, reflect the X-rays; and the reflected rays emerge at the same angle, and so reinforce one another, when the angle of incidence,  $a$  (Fig. 25), of the X-rays is such that  $l = 2d \sin a$ . Here  $l$  represents the wave-length of the X-rays,  $d$  is the distance between the successive layers of atoms in the crystal, and  $a$  is the angle of incidence. Since  $l$  and  $a$  are known,  $d$  can be calculated. By this means one can determine the distance

between the layers in different directions, and so measure the dimensions of the crystal lattice.

The human eye is not constructed so as to be able to detect X-rays, and a photographic plate or the property of X-rays of making the air a conductor for electricity must be utilised in order to detect the path of the reflected beam.

When a crystal of diamond, which is built up of atoms of carbon, is examined by means of X-rays, it is found that the atoms are arranged in such a way that each is at the centre of a regular tetrahedron, and is joined to four other atoms which lie at the corners of the tetrahedron. A representation of this arrangement is shown in Fig. 26. The atoms are spaced at equal distances from one another, the distance between two neighbouring atoms being 1.54 Ångström units, 1 Ångström unit being equal to the one hundred millionth of a centimetre ( $1 \times 10^{-8}$  cm.).

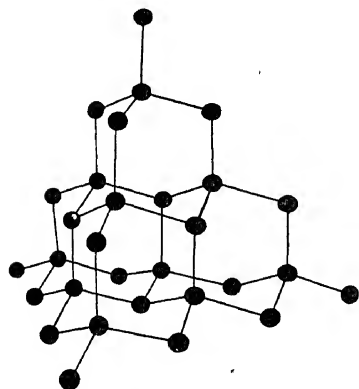


FIG. 26.—Arrangement of atoms in the diamond crystal.

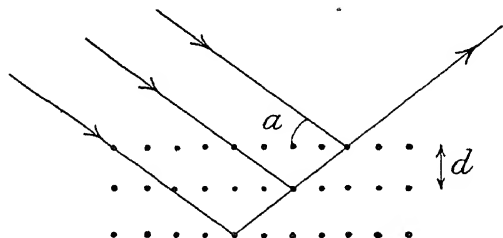


FIG. 25.—X-ray examination of crystals.

On looking at the model of the diamond crystal one is struck by the fact that the atoms in any particular layer are arranged in groups of six, forming a series of regular hexagons. This grouping of carbon atoms which X-rays have revealed in the crystal of the diamond, had already been inferred by chemists. In the case of the compound benzene,  $C_6H_6$ , one of the constituents of coal-tar, chemists had long puzzled over the way in which the

six carbon and six hydrogen atoms are joined together in the molecule; and the German chemist, Kekulé, as we shall learn more fully later, suggested, as far back as 1867, that the six carbon atoms are joined together to form a hexagonal "ring," and that one hydrogen atom is attached to each of the carbon atoms. This arrangement was suggested in order to account for the chemical behaviour of benzene, and X-ray examination has shown that the hypothesis is well-founded; for such examination

has revealed the fact that the molecule has the shape of a regular hexagon the thickness of which is  $1.19 \times 10^{-8}$  cm., and the length of the sides,  $6.02 \times 10^{-8}$  cm. One cannot but be amazed at the way in which the wonderful imaginative vision of the chemist has been confirmed by the experimental investigations of the physicist.

In the case of common salt (sodium chloride), a compound which is formed, as we have seen, by the combination of a positively charged sodium atom with a negatively charged chlorine atom, the crystals have the form of a cube; and X-ray examination demonstrates that the electrically charged sodium and chlorine atoms or ions, as they are called, are arranged as indicated by the model shown in Fig. 27. Each sodium atom is attached to six chlorine atoms, and each chlorine atom, similarly, is attached to six sodium atoms.

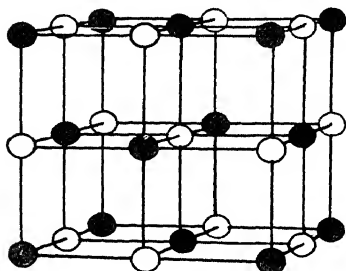


FIG. 27.—Arrangement of atoms in the crystal of sodium chloride.

By means of the X-ray examination of crystals, physicists are unravelling the intimate structure of crystals; and it is now possible, in many cases, to infer and to represent by means of models, the designs of nature's architecture. Here, however, the units of measurement are not the foot and the yard but the hundred millionth part of a centimetre.

## CHAPTER IX

### THE DETERMINATION OF ATOMIC WEIGHTS

THE atomic theory, which was promulgated by Dalton in the early years of the nineteenth century, afforded, as we have seen, a reasonable explanation of the fundamental and experimentally verified laws of chemical combination by weight—the law of fixed and the law of multiple proportions. These laws, that is to say, became intelligible if one assumed that the ultimate particles of matter are the atoms of the different elements, and that compounds are formed by the union of these atoms. The atomic hypothesis, moreover, by postulating that the atoms have definite weights or masses, different in the case of different elements, not only made it possible to give a quantitative as well as a qualitative explanation of the laws of combination, but provided also a means by which the hypothesis itself might be tested.

For the verification and practical application of the atomic theory, it was, however, clearly necessary to determine the atomic weights or the relative weights of the atoms of the different elements which were, according to the theory, the fundamental units of chemical science; and this work was taken up with great energy and ability by *BERZELIUS*, to whom we owe the first reasonably accurate determinations of atomic weights. "I recognised," wrote *Berzelius*, who with great scientific insight appreciated the value of the Daltonian hypothesis, "that if the newly-arisen light was to spread, it would be necessary to ascertain, with the utmost accuracy, the atomic weights of all elementary substances, and particularly those of the more common ones. Without such work, no day would follow the dawn. This was therefore the most important object of chemical investigation at the time, and I devoted myself to it with unrelenting labour."

In spite of the labour of *Berzelius*, however, interest in the atomic theory waned greatly during the first half of the nineteenth century, owing mainly to the confusion which reigned regarding the distinction to be drawn between atomic weights

and the proportions in which elements combine to form compounds; and it was not till about 1860 that chemists recognised in the molecular theory propounded by Avogadro as early as 1811, a sure basis on which to found atomic weights. From that time one may date the general appreciation by chemists of the importance of Dalton's theory, and the full recognition of atomic weights as essential constants of chemistry. Thereby, also, the era inaugurated by Lavoisier reached its full development and chemistry became firmly established as an exact science.

Although the atomic weights of elements can, as has already been pointed out (p. 90), be determined by the method of positive ray analysis, and although it is now recognised that the atomic weights, determined by the methods of chemical analysis, are frequently only average values for mixtures of isotopes, yet these chemically determined atomic weights are of supreme value. In all the practical operations of chemistry, in the analysis and production of compounds whether in the scientific laboratory or in the industrial factory, it is the chemical atomic weights which interest us, for it is on them that depend the quantitative relations between elements which govern the production of compounds.

**Equivalents.**—All chemical methods of determining the atomic weights of the elements depend on the accurate determination of the composition of compounds; that is to say, on the determination of the exact proportions in which the different elements combine. By the analysis of water, for example, it has been found that this substance is formed by the combination of the two elements, hydrogen and oxygen, in the proportions of 8.00 parts of oxygen to 1.008 parts of hydrogen by weight. Similarly, when the metal copper is heated in a current of oxygen, combination takes place and a black oxide of copper is formed. Analysis shows that in this compound 8.00 parts of oxygen are combined with 31.785 parts of copper. By analysing the compounds of oxygen with the different elements, then, we shall clearly be able to draw up a table showing the proportions by weight in which the different elements combine with a definite proportion by weight of oxygen. We arrive thereby at the idea of *equivalence* among the elements; and if we take as our standard of reference, 8 parts by weight of oxygen,<sup>1</sup>

<sup>1</sup> Formerly, when the atomic weight of hydrogen was taken as the standard and put equal to unity, equivalents were referred to 1 part by weight of hydrogen. On this basis, the atomic weight of oxygen was 15.88 and the equivalent, 7.94. Since, however, atomic weights are now referred to the atomic weight of oxygen as standard, the value of which is taken as 16.00, the standard of equivalents is taken as 8.00 parts by weight of oxygen.



we can define the *equivalent* of an element as the number of parts by weight of an element which will combine with, or which can replace in its compounds, 8 parts by weight of oxygen. The equivalent, let it be noted, is not a definite weight but a number, representing a relative weight or a ratio. Using the above standard, the equivalent of hydrogen is 1.008, of copper 31.785, of sodium 23.00, etc.

So far, the matter is simple; and if it could justifiably be assumed that all compounds are formed by the combination of only one atom of each element, then the value of the equivalent would also be the value of the atomic weight, with the atomic weight of oxygen equal to 8. Unfortunately, however, for the early adherents of the atomic theory, nature does not work according to so simple a plan. Moreover, elements may combine in more than one proportion, as Dalton had already discovered, and may therefore have more than one equivalent. Copper, for example, can form two compounds with oxygen in one of which 31.785 parts of copper are combined with 8 parts by weight of oxygen; and in the other, 63.57 parts of copper are combined with 8 parts of oxygen. The atomic weight will obviously be equal to the equivalent or to some multiple of the equivalent, but without some further information, without a knowledge, for example, of the number of atoms of copper and oxygen which combine to form a molecule of each compound, it is impossible to decide what multiple of the equivalent is to be taken as the atomic weight. The number of variables is too great.

To overcome the difficulty which was met with, Dalton made various assumptions—for which, however, there was no real justification—whereas Berzelius was guided in his choice of atomic weights by another set of rules, which in some cases led to atomic weight values different from those obtained by Dalton. Confusion reigned. Some chemists gave up the attempt to determine atomic weights and contented themselves with equivalents (in spite of the fact that some elements have more than one equivalent), and other chemists lost interest in the atomic theory altogether. Although great progress was made in the accurate determination of equivalents, more especially by the French chemist, JEAN BAPTISTE DUMAS (1800–1884), the Swiss chemist, JEAN CHARLES DE MARIGNAC (1817–1894), and the Belgian chemist, STAS, different meanings were given by different chemists to the terms equivalent, atomic weight and molecular weight, and no agreement existed with regard to the formulæ of different compounds.

At length, in 1860, recourse was had to a congress, to a round

table conference of the leading chemists of the day, which assembled at Karlsruhe, in Germany, in order to reach, if possible, an agreement regarding symbols and formulæ. The conference failed entirely in its object, but each member carried away with him a copy of a *Sketch of a Course of Chemical Philosophy held in the Royal University of Genoa*, drawn up in 1858 by the Italian patriot and chemist, STANISLAO CANNIZZARO (1826-1910), himself a member of the Karlsruhe conference.



STANISLAO CANNIZZARO IN 1858.

(Reproduced from a portrait by D. Salorson by permission of the Chemical Society, from the *Journal of the Chemical Society*, 1912.)

A Sicilian by birth, Cannizzaro took part in the rebellion of 1847, and again, in 1860, while Professor of Chemistry in the University of Genoa, he joined Garibaldi and his famous Thousand in Palermo. In 1861, Cannizzaro was called to the Chair of Chemistry in the University of his native town, Palermo. Ten years later he became Professor of Chemistry in the University of Rome, and was at the same time made a Senator of the Kingdom. Cannizzaro made many contributions to the chemistry

of the compounds of carbon, and after chemists had been wandering for fifty years in the mists of false and confused ideas, it was he who through his clear-sighted recognition of the meaning and importance of Avogadro's hypothesis, came to lead them out of the wilderness.

It was, then, while at Genoa that Cannizzaro drew up the *Course of Chemical Philosophy* which cleared away all the existing confusion by reviving the hypothesis of Avogadro which had been ignored ever since 1811, and by showing how this hypothesis and the determinations of molecular weight which were founded on it, formed a firm basis for the determination of atomic weights. The reading of Cannizzaro's pamphlet brought conviction more or less quickly to all, most quickly, perhaps, to Lothar Meyer, who wrote: "It was as though scales fell from my eyes, doubt vanished, and was replaced by a feeling of peaceful certainty."

**Molecular Weights as a Basis for Atomic Weights.**—It has already been pointed out that on the basis of the hypothesis of Avogadro (p. 108), the molecular weight of a substance in the state of gas or vapour can be calculated from determinations of the gas or vapour density. But, as Cannizzaro pointed out, if the molecular weights of a series of compounds containing a given element be determined, the quantities of that element contained in the molecular weights of the different compounds are always whole multiples of the smallest quantity; and this quantity, therefore, represents the atomic weight of the given element, for an atom is the smallest amount of an element which can take part in the formation of a molecule.

By analysing and determining the molecular weight (see pp. 109 and 110) of a number of gaseous or volatile compounds of hydrogen, for example, the following table can be drawn up:

Substance.	Molecular weight.	Parts by weight of hydrogen contained in the weight of the substance
Hydrogen chloride . . . . .	36.468	1.008
Hydrogen bromide . . . . .	80.928	1.008
Phosphine (hydrogen phosphide) . . .	34.064	3.024
Water vapour . . . . .	18.016	2.016
Methane (Marsh gas) . . . . .	16.032	4.032

From this table it is clear that in no case is the amount of hydrogen in the molecular weight of its compounds less than 1.008 parts, and, where the proportion is greater, the higher proportions are whole multiples of 1.008. This holds, moreover, not only for the compounds mentioned in the above table but for all compounds of hydrogen so far tested—amounting to

many thousands in number. We can, therefore, without doubt or ambiguity, take 1.008 as the atomic weight of hydrogen.

In a similar manner, by analysis and determination of molecular weights, the atomic weights of other elements may be determined; and it will therefore readily be understood how a sure decision regarding the atomic weights of those elements, at least, which are capable of forming volatile compounds, can be reached.

The molecular weight values which are given in the preceding table for the purpose of illustration are not the results of direct molecular weight determinations. Except in a few cases, the determination of the gas density or vapour density cannot be carried out with an accuracy which is sufficiently great to allow of the direct calculation of atomic weights. Determinations of the vapour density, therefore, and the calculation therefrom of molecular weights which are only approximately correct, are carried out and are of value mainly for the purpose of enabling a decision to be made as to what multiple of the equivalent of an element should be taken as the atomic weight. It is the accurate determination of the equivalent that is the real foundation of atomic weight determinations.

**Atomic Heat.**—Before the determinations of molecular weight, based on the hypothesis of Avogadro, had been recognised as a reliable method of deciding atomic weight values, another method, applicable to solid elements and more especially to the metals, was introduced in 1819 by the French physicists, PIERRE LOUIS DULONG (1785–1838) and ALEXIS THÉRÈSE PETIT (1791–1823). The amount of heat in calories<sup>1</sup> which must be added to 1 gram of a substance, in order to raise the temperature by 1° C., is called the *specific heat* of the substance; and Dulong and Petit found that *when the specific heat is multiplied by the atomic weight, the quotient is approximately constant for the different solid elements* (Dulong and Petit's law). Later investigations have shown that although there are a few marked exceptions (carbon, boron, silicon, etc.), the values obtained for the product of specific heat and atomic weight (the so-called *atomic heat*) vary mostly within comparatively narrow limits—mostly between 6 and 7—and have an average value of about 6.4. This approximate law, therefore, may be used to decide which multiple of the equivalent is to be taken as the atomic weight. One example of the application of this rule will suffice.

Copper, we have seen, can form two compounds with oxygen. On analysing these compounds the two equivalents 31.785 and

<sup>1</sup> One calorie is the amount of heat required to raise the temperature of 1 gram of water 1° C.

63.57 are found. The specific heat of copper is 0.0923. Therefore the *approximate* value of the atomic weight is given by the expression :

$$\text{Approximate atomic weight} = \frac{6.4}{0.0923} = 69.3.$$

The correct atomic weight is, therefore,  $31.785 \times 2 = 63.57$ .

The factor by which the equivalent must be multiplied in order to give the atomic weight, represents what has been called the valency of the element (p. 66).

**Calculation of Formulæ.**—A knowledge of atomic weights enables one to calculate the formula of a compound from the percentage composition obtained by analysis. For example. Analysis shows that in 100 parts by weight of water, there are 11.19 parts of hydrogen and 88.81 parts of oxygen; or, the percentage composition of water is 11.19 per cent. of hydrogen and 88.81 per cent. of oxygen. If, now, one divides these two numbers by the respective atomic weights of the elements, one obtains the *relative number of atoms* of either element in the compound. Thus, we have :

$$\frac{11.19}{1.008} = 11.10 \quad \text{and} \quad \frac{88.81}{16.00} = 5.55.$$

In a molecule of water, therefore, the *relative number* of atoms of hydrogen and oxygen is as 11.10 to 5.55; or, as 2 is to 1. The molecule of water may therefore be written  $\text{H}_2\text{O}$ . Since, however, one is dealing only with relative numbers the formula might also be  $\text{H}_4\text{O}_2$ ,  $\text{H}_6\text{O}_3$ , or, generally,  $(\text{H}_2\text{O})_x$ . The formula  $\text{H}_2\text{O}$  is merely the simplest formula calculated from the analysis, the so-called *empirical formula*; and in order that we may obtain the true formula of the molecule, it is necessary to know the molecular weight. Since water is a volatile liquid, it can be vaporised, and the density of the vapour determined. When this is done, it is found that 22.4 litres of water vapour at N.T.P., would, if it could be obtained under these conditions,<sup>1</sup> weigh about 18.5 grams. The determination is not very accurate as we have learned, but sufficiently accurate to show that the molecular weight is in the neighbourhood of 18. If we examine the formula  $\text{H}_2\text{O}$ , we find that this gives a molecular weight of  $2.016 + 16.00 = 18.016$ . We conclude, therefore, that this is the true formula for a molecule of water in the state of vapour.

<sup>1</sup> The volume of a given weight of water vapour is determined at a temperature above  $100^\circ \text{C}$ , and the volume at N.T.P. then calculated according to the laws of Boyle and Gay-Lussac.

## CHAPTER X

### THE GASES OF THE ATMOSPHERE AND THE PHENOMENON OF COMBUSTION

**Historical.**—Air, the gaseous envelope or atmosphere<sup>1</sup> by which the earth is surrounded, was regarded by the Greek philosopher Anaximenes, in the sixth century B.C., as the universal principle underlying all matter, and was one of the four elements of Aristotle and of the Schoolmen of the Middle Ages. Although invisible, the winds made known its existence to man, and even the ancient Egyptian craftsmen knew how to make use of it in their primitive bellows (Fig. 28); while direct proof of its

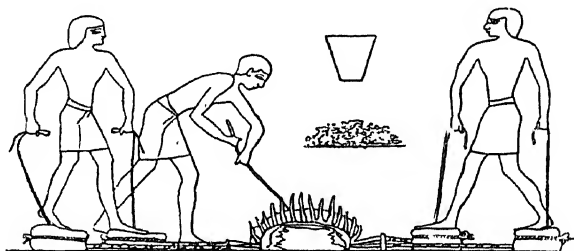


FIG. 28.—Foot-bellows used in ancient times by Egyptians.

material nature was given when Galileo, in 1632, determined the weight of a given volume. As the most accurate determinations now show, 1 litre of dry air at N.T.P., weighs 1.293 gram. It is, therefore, 14.375 times heavier than an equal volume of hydrogen.

Although from earliest times air had been regarded as a simple and single substance, a different view began to be held in the seventeenth century; and from a study, more especially, of the calcination of metals such as lead and tin, and of the phenomenon of burning or combustion, chemists were led to the conclusion that air is a mixture. For more than a century, from the time of Boyle to the time of Lavoisier, the greater part

<sup>1</sup> From the Greek *ἀτμός* (atmos), vapour, and *σφαῖρα* (sphaîra), sphere.

of chemical investigation centred round the problem of combustion and the composition of the air; and the work of the great experimentalists and founders of "pneumatic chemistry," Black, Scheele, Priestley and Cavendish, more especially, was guided by the first great, but erroneous, theory of chemical action, the phlogiston theory of combustion. It was in terms of this theory, also, that the results obtained by these investigators were expressed. It was a period full of interest; a period in which we can see chemistry passing somewhat slowly and jerkily out of mediævalism and developing into a rational science. In this period we see how, in order to account for observed phenomena, a theory is put forward which, albeit erroneous, serves its purpose of interpreting the results of observation; and we also see how this theory, after having captured the minds of men, is finally driven from its fastness by the irresistible force of new facts with which it is no longer able to contend.

The fact that metals such as lead and tin, when heated in the air, change into an earthy material or *calx*, as it was called, was well known in the seventeenth century, as also was the fact that the *calx* which was formed weighed more than the original metal. Although it was recognised by the French physician, JEAN REY (1575-1645), in 1630, as well as by the English scientist, ROBERT HOOKE (1635-1703), that the air, or a portion of it, takes part in the process of calcination, it was the young doctor of Bath, JOHN MAYOW, who came nearest to giving a correct explanation of the process of combustion and of the process of animal respiration.

Born in London in 1645, JOHN MAYOW, after taking his degree in law at Oxford, became a medical practitioner at the fashionable health resort, Bath. While there, he published, in 1674, his famous *Tractatus Quinque Medico-Physici*, in which he set forth his views on the nature of combustion and of animal respiration. Five years after the publication of these essays, in 1679, while still only in his thirty-fourth year, Mayow died and was buried in "the handsomest barn in England," the Church of Saint Paul, Covent Garden, London.

In his study of the phenomenon of combustion, Mayow inverted a large glass globe over water contained in a flat dish, and by means of a glass tube, through which air could pass, secured that the level of water inside and outside the flask was the same (Fig. 29). By means of a "burning glass," a piece of camphor in contact with a piece of tinder which had been

placed on a metal plate suspended in the flask, was ignited. After a time, the camphor ceased to burn and the level of the



JOHN MAYOW.

water rose, showing that the volume of air in the flask had been diminished. Failing to bring about the ignition of another piece of camphor in the same flask, Mayow concluded therefrom that the residual air was no longer able to support combustion. A similar experiment was carried out with a burning candle.

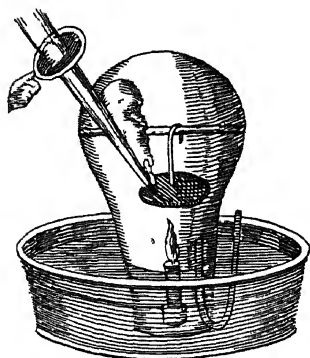


FIG. 29.—Mayow's apparatus.

From these experiments, Mayow inferred that the particles of the air are associated with a *spiritus nitro-aereus* or nitro-aerial spirit, which is necessary for the combustion of inflammable substances. Mayow does not seem to have regarded the nitro-aerial spirit as a definite gaseous substance—at that time chemists had not yet learned to distinguish between different gases—but rather as particles attached



to the aerial particles and derived from the sun; and, according to him, combustion consists of a violent reaction between the combustible substance and the nitro-aerial particles. The appearance of fire was interpreted as due not to the ardour of chemical union but to the interplay of hostile and warring particles.

By the process of combustion, the air was deprived of its nitro-aerial spirit, and so became unable further to support combustion. Moreover, the increase of weight which, as Mayow observed, takes place when metallic antimony is burned, must be due to the absorption of the nitro-aerial particles.

Just as nitro-aerial spirit is necessary for combustion, so also, as Mayow showed, it is necessary for life; for if a mouse is enclosed in a flask of air over water, the volume of air is found to diminish and after a time the mouse dies. The residual gas is incapable of supporting life.

From the fact that a mixture of charcoal, sulphur and nitre (gunpowder) burns with great vigour even under water, and therefore out of contact with the air, Mayow inferred the presence in the nitre of nitro-aerial spirit in a very condensed form.

The explanation of combustion which was thus put forward by Mayow in 1674 was a long step towards the true explanation put forward by Lavoisier a century later. It failed to carry conviction, however, for it was linked too much to the alchemistic idea of principles and essences, and it lacked the support of exact quantitative analysis. These deficiencies, doubtless, would soon have been made good had Mayow's short life been prolonged even a few more years or if his contemporaries, including the illustrious Boyle, had had sufficient insight to realise the importance of the views which he propounded. Mayow, still comparatively young, did not have that standing in science which could compel a due consideration of his views, and these were ignored or rejected in favour of an erroneous and to us fantastic theory due mainly to the German chemist, GEORG ERNST STAHL (1660-1734), who was born at Ansbach and became, in 1693, Professor of Medicine and Chemistry in the University of Halle.

**The Phlogiston Theory.**—One of the leading teachers of chemistry of his time, Stahl owed his influence in science mainly to the so-called *Phlogiston Theory*, which he propounded in explanation of the process of combustion. According to this theory, which in its essence reaches back to the philosophy of ancient Greece, all combustible substances, including also the

metals which form calces on being heated in air, contain an inflammable principle or principle of combustibility, akin to the "sulphur" of the Mediæval alchemists, and the *terra pinguis* or "fatty earth" of Stahl's master, JOHANN JOACHIM BECHER (1635-1682). To this principle of combustibility Stahl gave the name *phlogiston*;<sup>1</sup> and it was assumed that when a substance burns, this phlogiston escapes, leaving behind, as in the case of the metals, the ash or calx. The air was regarded merely as an absorbent or solvent for the phlogiston, which, in the absence of such an absorbent, could not escape. According to this theory, a metal was regarded as being a compound of a calx and phlogiston, and therefore if the calx were recombined with phlogiston, the metal would be regenerated. This recombination could be brought about by heating the calx with charcoal, a material which burns leaving practically no ash and which was therefore regarded as being almost pure phlogiston.

For a hundred years the phlogiston theory was accepted by chemists (so little had the teaching of Boyle been taken to heart), and the long life of such an erroneous theory may be attributed to the fact that chemistry was, at that time, largely a qualitative and descriptive science. Form rather than weight, it was considered, was the characteristic property of substances. The balance, of course, was known and used, but its importance was not fully appreciated; so that when it was found that the products of a combustion weigh more than the original combustible substance, the upholders of the phlogiston theory sought to defend their position by identifying phlogiston with the principle of levity. The escape of the principle of levity from the body left the body heavier.

Much as we may be inclined to smile at such an explanation, we must remember that the phlogiston theory served successfully its day and generation, and satisfied even the modern requirements of a theory, in that it gave an explanation of combustion which satisfied men's minds at the time, and was capable of explaining facts of a diverse kind and even of predicting new facts. The phlogiston theory, however, long outlived its usefulness, and the tenacity with which it maintained itself is an instructive illustration of the difficulty which most men have of freeing their minds from the authority of a long-held theory; and it conveys a warning, which is not unnecessary even at the present day, that a theory which serves at first to illumine the path of advance may at length so dazzle the eyes that they fail to observe the facts. As Priestley wrote: "We may take a maxim so

<sup>1</sup> From the Greek verb *φλογίζειν* (phlogizein), to burn.

strongly for granted that the plainest evidence of sense will not entirely change, and often hardly modify, our persuasions." In science, this is a danger of which to beware, for, as the German chemist Liebig wrote, many years ago, after having been a victim of the misfortune to which he refers: "No greater misfortune could befall a chemist than that of being unable to shake himself free from the power of preconceived ideas, and, yielding to the bias of his mind, of seeking to account for all phenomena which do not fit in with these ideas by explanations which have no basis in experiment."

At the present day it is difficult to understand wherein lay the power of the phlogiston theory which could so completely hold in thrall the minds of such intellectually brilliant men as the great experimentalists to whom reference has already been made—Scheele, Priestley and Cavendish. Convinced phlogistonists though they remained to the end of their lives, they contributed in great measure through their experimental work, culminating in the discovery of oxygen by Scheele and by Priestley, to the overthrow of the theory from which they were themselves unable to break free.

Although Scheele, who undertook a systematic investigation of the process of combustion, was led to the conclusion that atmospheric air consists of two gases—"fire-air" and vitiated air (nitrogen)—his attachment to the theory of phlogiston and his failure to carry out his experiments in a quantitative manner, prevented him from arriving at that real understanding of the process of combustion and knowledge of the composition of the air which we owe to the brilliant French chemist, of whose life an account has already been given (p. 50), ANTOINE AUGUSTE LAVOISIER.

**Lavoisier and the Overthrow of the Phlogiston Theory.**—Even as early as about 1764, Lavoisier had observed, as others before him had done, that when sulphur or phosphorus is burned in air, the product of combustion weighs more than the combustible body, and, like his predecessors, Mayow and the Russian chemist Michael Vassilievitch Lomonossov (1711–1765), he attributed the increase of weight to something taken from the air. He advanced beyond his predecessors, however, in that he showed, by actual experiment, that in the case of tin the increase in weight of the metal on being heated in air is equal to the weight of "air" absorbed, and was therefore not due to the passage of "fire matter" through the walls of the vessel, as Boyle had thought. Since Lavoisier had shown, not only qualitatively but also quantitatively, that in the process

of calcination only a portion of the air combines with the metal, the only remaining step to be taken was to recover again from the calx the gas which had been removed from the air, and so to ascertain its nature. It was at this point that Priestley made his great contribution to the overthrow of the theory of phlogiston in which he was a lifelong believer.

During a visit to Paris in the autumn of 1774, Priestley, while dining with Lavoisier, mentioned his discovery of the gas now known as oxygen; a gas which he had obtained by heating *mercurius calcinatus per se*, or oxide of mercury as it is now called, and in which a candle burned much better than in common air. The importance of this discovery was at once recognised by Lavoisier, who conceived the idea that this new gas represented the portion of the air which combines with a metal and gives rise to the calx. The correctness of this idea was proved by a

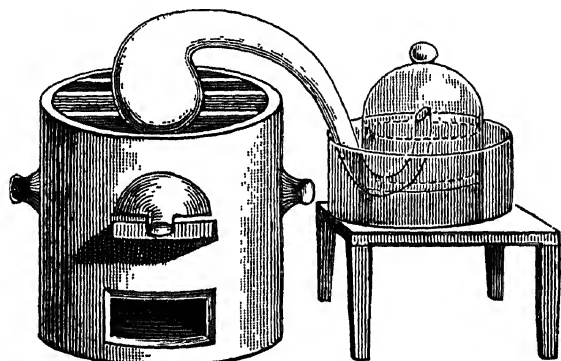


FIG. 30.—Lavoisier's experiment of heating mercury in air.

quantitative experiment which has become one of the great classical experiments of chemistry.

The calx of mercury (oxide of mercury) was first synthesised by heating a weighed amount of mercury in a retort which communicated with a known volume of air contained in a bell-jar standing over mercury (Fig. 30). The mercury in the retort was heated on a charcoal furnace for twelve days to a temperature just below its boiling-point. At the end of this time, a quantity of red calx of mercury, 45 grains in all, had formed on the surface of the metal, and the volume of air in the bell-jar had diminished by 7–8 cubic inches. The residual gas in the bell-jar did not support life or combustion.

The red calx of mercury was then heated, and Lavoisier found that from 45 grains of the calx, 41 grains of metallic mercury were formed, and 7–8 cubic inches of a gas were evolved.

This gas was found to be "eminently respirable" and to support combustion better than air.

By these and other experiments, Lavoisier proved conclusively that the air consists essentially of two gases, now known as oxygen and nitrogen, and that when metals are calcined or substances are burned in air, the oxygen of the air combines with the metal or burning substance. In other words, *the process of combustion is a chemical reaction, a chemical combination of the combustible substance with the oxygen present in the air, the process being accompanied by emission of heat and, it may be, also of light.* The nitrogen of the air takes no part in the process, but acts merely as a diluent which moderates the vigour of the combustion.

**The Gases of the Atmosphere.**—Atmospheric air is a *mixture* of a number of different gases in proportions which, so far as the main constituents are concerned, remain remarkably constant not only at different times and seasons of the year but also at different parts of the earth's surface. The gases normally present in air are: nitrogen, oxygen, carbon dioxide, water vapour and a group of gases, known as the rare gases, the most abundant of which is argon. Besides these normal constituents of the air, other gases and solid particles, derived from local sources, are present as what we may call impurities.

**Nitrogen.**—In 1772, DANIEL RUTHERFORD (1749–1819), a pupil of Joseph Black at the University of Edinburgh, where he later became Professor of Botany, showed, in apparently the only piece of chemical investigation which he ever carried out, that when white phosphorus is burned in air, acid fumes are formed; and when these are removed by alkali, the volume of air is found to have diminished and the residual gas no longer supports combustion. In this way, the gas now known as **nitrogen** was discovered.<sup>1</sup>

In this reaction, as we now know, oxygen is removed from the air by the phosphorus, and nitrogen (along with the rare gases) is left, and if carried out with appropriate precautions the reaction can be employed for the purpose of determining the proportion of oxygen in the air. When the residual gas, which is a mixture of nitrogen and the rare gases, is passed over heated magnesium metal, the magnesium combines with the nitrogen to form a compound known as magnesium nitride, while the rare gases remain free,

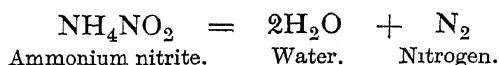
<sup>1</sup> The credit of discovering nitrogen must be shared with Cavendish, for it is known that in a private letter to Priestley he communicated the preparation of the gas by passing air repeatedly over red-hot charcoal and absorbing the resulting carbon dioxide in potash.

As the result of analysis it is found that the average composition of purified air, free from carbon dioxide and water vapour, is as follows :

	Per cent. by volume.	Per cent. by weight
Nitrogen . . . . .	78.06	75.5
Oxygen . . . . .	21.00	23.2
Rare gases . . . . .	0.94	1.3

Nearly four-fifths of the air, by volume, therefore, consists of nitrogen, and one-fifth of oxygen.

The gas which Rutherford and, after him, Scheele and Lavoisier obtained by the removal of oxygen from air, was, as we shall learn more fully later, not pure nitrogen, although until 1894 it was thought to be so. The pure gas, however, can be obtained by the decomposition of certain nitrogen-containing compounds, such as ammonium nitrite, a substance which can be represented by the formula  $\text{NH}_4\text{NO}_2$ . When this salt is carefully heated, decomposition takes place into water and nitrogen, as represented by the equation :



At the present day very large quantities both of nitrogen and of oxygen, in a nearly pure state, are produced industrially by the fractional distillation of "liquid air," which consists of a mixture of liquid nitrogen (together with the rare gases), and liquid oxygen, the boiling-points of which are  $-196^\circ \text{C}$ . and  $-183^\circ \text{C}$ . respectively. By distilling the liquid air in a suitable apparatus, it has been found possible to effect an almost complete separation of the gases.

Although, as we shall learn more fully later, nitrogen plays a rôle of very great importance in the economy of nature, it is a very inert or chemically inactive element at the ordinary temperature. As has already been stated, it does not support combustion, nor does it support life. For this reason it was called *azote*<sup>1</sup> by Lavoisier—a name still used in France. The name nitrogen<sup>2</sup> (*nitrogène*), by which the element is known in English-speaking countries, was suggested in 1790 by the French chemist, JEAN ANTOINE CHAPTAL (1756–1832)—"an active, amusing, intriguing courtier and chemist"<sup>3</sup>—who after acting as Professor of Chemistry in the University of Montpellier and at the Ecole des Arts in Paris, became Minister of the

<sup>1</sup> From the Greek  $\alpha$  (alpha), not, and  $\zeta\omega\eta$  ( $zōē$ ), life.

<sup>2</sup> From  $\nu\acute{\iota}\tau\rho\omicron\nu$  (*nitron*), nitre, and  $\gamma\epsilon\nu\nu\acute{\alpha}\omega$  (*gennao*), I produce.

<sup>3</sup> Sir Humphry Davy.

Interior under Napoleon, and was by him created Comte de Chanteloup. In 1819, he was made a Peer of France by Louis XVIII.

The discovery of **oxygen** we owe to two men of a very different type, mentally and temperamentally, Scheele and Priestley.

CARL WILHELM SCHEELLE was born at Stralsund, in what was then Swedish Pomerania, on December 9th, 1742, and at the age of fourteen became apprenticed to an apothecary in Gothenburg. While there, and later at Malmö and Stockholm, he devoted all



*Carl Wilhelm Scheele.*

his available time to the study of chemistry, and manifested not only extraordinary energy but great intellectual power and aptitude for experiment. In 1770, he went to Upsala, where he continued his experimental investigations and composed his classical *Treatise on Air and Fire*, in which he discussed the phenomenon of combustion and the composition of the air. It was at Upsala, also, in 1773, that he first obtained oxygen by heating nitre, red oxide of mercury and other substances, although it was not till 1777 that his discovery was published. Scheele, apparently, was unacquainted with the "pneumatic

trough," and collected the gas in a bladder tied to the mouth of a retort (Fig. 31).

Apart from the discovery of oxygen, Scheele also discovered chlorine and made many other important contributions to

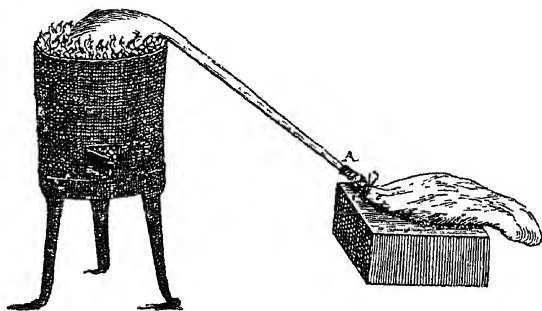


FIG. 31.—Scheele's apparatus for the preparation of oxygen.

chemistry. Recognised and appreciated as one of the foremost chemists of the time, he died in 1786 at Köping, where he had, since 1775, carried on business as an apothecary.

In Scheele, contending with poverty and ill-health, we have the type of the scientific specialist and "poor scholar," who



Scheele's house at Köping.

(From *Skandinavisches Archiv für Physiologie*, 1926.)

found all his interests in, and devoted all his energies to the pursuit of scientific knowledge, enthusiastically declaring: "It is the truth alone that we desire to know, and what joy there is in discovering it!" In Priestley, on the other hand, we



have the intellectually brilliant amateur who pursued science as a hobby in the leisure moments of a life which was full of wide and varied interests.

JOSEPH PRIESTLEY, one of the most versatile, eager and intellectually active men of the eighteenth century, was born at Fieldhead, in the parish of Birstall, near Leeds, in 1733. At the age of twenty-two, he became a minister of the English Presbyterian Church, and later, in 1761, tutor in classics at a new Academy which was opened at Warrington. In 1767, he became minister of Millhill Chapel, Leeds, and, in 1772, "lite-



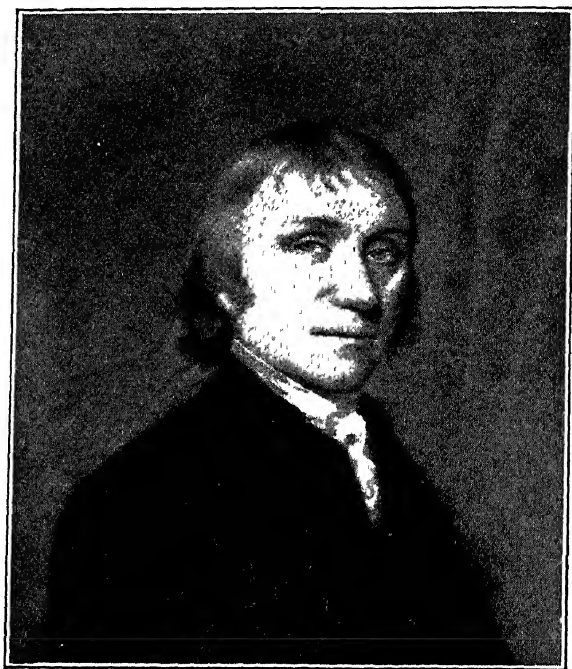
Priestley's birthplace.

(After a drawing by J. A. Symington. From *Thorpe's Life of Priestley*, by permission of Messrs. J. M. Dent & Sons, Ltd.)

On the front of the cottage which now occupies the site of Priestley's birthplace (on the left of the illustration), is a tablet with the inscription: Joseph Priestley, Discoverer of Oxygen, was born on this site, A D 1733.

rary companion" to Lord Shelburne, who afterwards became the first Marquis of Lansdowne. It was while occupying this apparently not very exacting post that Priestley carried out some of the most important of his chemical experiments. In 1780, Priestley settled in Birmingham as minister of the New Meeting House, the leading Unitarian Chapel of the town. During his residence there, Priestley made his influence widely felt, and, whether by his preaching or by the numerous controversial writings which he published, he never rested in the propagation of the advanced philosophical and theological views which he held. A sympathiser with the French revolutionists and an outspoken

opponent of the doctrines and creeds of the Established Church, Priestley drew down on himself the anger of the people; and when, on the 14th of July, 1791—the anniversary of the taking of the Bastille and the outbreak of the French Revolution—some of Priestley's friends celebrated the occasion by a public dinner (at which, however, Priestley was not present), the fury of the populace broke out in what are known as the Birmingham Riots. For three days the town was given over to scenes of



JOSEPH PRIESTLEY.

brutality and mad passion, and Priestley, on whose house an early raid was made, was enabled to escape in time only by the help of some of his friends. His house was burned, and his books and apparatus flung into the street. Some years later, in 1795, Priestley left England for America, where he received a kindly welcome. He was offered, but declined, the Professorship of Chemistry in the University of Philadelphia, and finally settled at Northumberland, Pennsylvania, where he died in 1804.

**Oxygen.**—The discovery of oxygen by Priestley may be traced to the fact that in the summer of 1774 he came into

possession of a burning lens, twelve inches in diameter and twenty inches focal length, with which, as he writes, he "proceeded with great alacrity to examine . . . what kind of air a great variety of substances, natural and factitious, would yield, putting them into vessels which [he] filled with quicksilver and kept inverted in a basin of the same." One of the substances



Priestley's house at Northumberland, Pennsylvania.

It was at this house, built by Priestley in 1796, that there assembled in 1874 a number of American chemists in order to celebrate the centenary of the discovery of oxygen, and to found an Association which, two years later, developed into the American Chemical Society, now the largest Chemical Society in the world.

he heated was oxide of mercury, which yielded a gas which we now know as oxygen.

The element **oxygen**<sup>1</sup> is best prepared, in small quantity, by heating the well-known salt, chlorate of potash or potassium chlorate, a compound of potassium, chlorine and oxygen. When this substance is heated, it undergoes decomposition, with production of oxygen and potassium chloride; and the decomposition takes place with much greater ease, that is, at a lower temperature, when certain finely divided substances; more especially

<sup>1</sup> This name, derived from the Greek *ὀξύς* (oxys), acid, and *γεννάω* (gennaō). I produce, was given to the gas by Lavoisier in the mistaken belief that the element is an essential constituent of all acids.

black oxide of manganese (manganese dioxide) or pyrolusite, are added to the chlorate. The use of pyrolusite for this purpose was first introduced by the German chemist, DÖBEREINER, in 1832.

The preparation is very conveniently carried out in the apparatus shown in Fig. 32. The mixture of chlorate and manganese dioxide is heated in a thin-walled glass tube, A, known as a *test-tube*, the mouth of which is closed by a cork through which passes a glass *delivery tube*, B. The end of this tube, through which the oxygen escapes, dips under the surface of water contained in a basin or "pneumatic trough"; and the gas can be collected in a cylinder or other vessel, C, which is filled with water and inverted over the open end of the delivery tube.

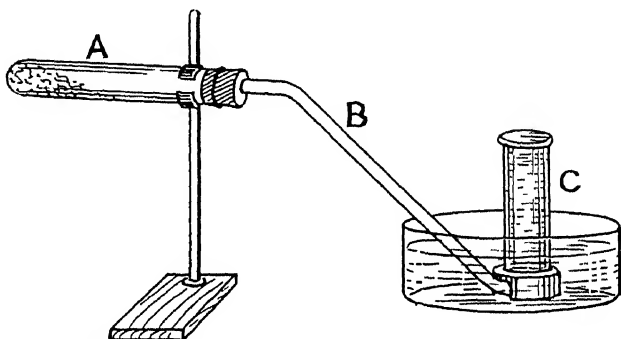
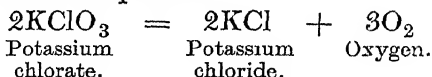


FIG. 32.—Preparation of oxygen.

The decomposition of the potassium chlorate can be represented by the chemical equation :



Translated into words this reads: Two molecular proportions (or, 245·12 parts by weight) of potassium chlorate yield two molecular proportions (or, 149·12 parts by weight) of potassium chloride, and three molecular proportions (or, 96 parts by weight) of oxygen; or, since 32 grams (1 gram-molecule) of oxygen occupies a volume of 22·4 litres at N.T.P., it follows that from 245·12 *grams* of potassium chlorate, 67·2 litres of oxygen at N.T.P., can, theoretically, be obtained.

The most conspicuous property of oxygen is the readiness with which it combines with other substances, as manifested, for example, in the vigour with which it supports combustion.<sup>1</sup>

<sup>1</sup> The fact that Priestley at first thought that oxygen was only a specially pure form of "dephlogisticated nitrous air" (nitrous oxide), which he had previously prepared, explains the words used by the poet Cowper in *The Garden*

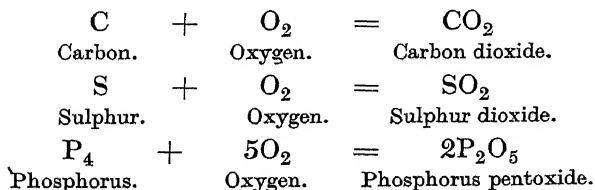
while the nitrous air  
Feeds a blue flame, and makes a cheerful hearth.

It was this property, as we have seen, which led to its identification as something different from ordinary air. That substances and materials which burn in air burn with greatly increased vigour in oxygen, is made strikingly manifest when a glowing piece of wood is thrust into a jar of the gas. Immediately, the glowing wood bursts into flame. Even a piece of charcoal burns in oxygen with a bright light if it has first been made to glow by being strongly heated in a flame. Sulphur, also, and, still more, phosphorus, burn with great vigour in oxygen, the light emitted by the burning phosphorus being of a dazzling brightness.

During the combustion of phosphorus, dense white fumes are produced, and if a little water be poured into the jar in which the combustion has taken place, the white fumes dissolve in the water. If a solution of the purple colouring matter, *litmus*—a vegetable dye derived from a species of lichen—is added to this solution, the colour is changed to bright red; a change which indicates the presence of an *acid*. A similar result is obtained with the product of combustion of sulphur, and, less markedly, with the product of combustion of charcoal (carbon). On the other hand, if a solution of slaked lime in water (known as *lime water*) be poured into the jar in which the charcoal was burned, the solution becomes milky in appearance—a change which will be explained later.

The experiments which have just been discussed show clearly that in the combustion of carbon, sulphur and phosphorus in oxygen, new substances are produced which are different from the substances which undergo combustion; and since one is dealing only with elements, the conclusion must be drawn that the new substances which are produced must be *compounds* of the carbon, sulphur and phosphorus respectively with the oxygen. Such compounds are known as *oxides*, and the process of combination with oxygen is spoken of as *oxidation*.

The reactions which take place in the above combustion or oxidation processes can be conveniently summarised in the equations:



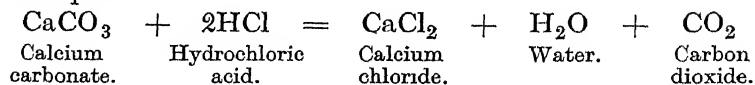
On investigating the physical properties of oxygen, it is

found that the gas dissolves only to a small extent in water, 1 litre of water at 0° C., dissolving no more than 48.9 c.c. of oxygen under the ordinary pressure; and at higher temperatures, the amount dissolved is still less. Nevertheless, even this small degree of solubility is of great importance, for it is on the dissolved oxygen that fish and other aquatic organisms depend for their supply of this vitally necessary element.

**Carbon Dioxide** is normally present in air to the extent of about 3 parts in 10,000 parts of air by volume, and although appreciable variations may be found at different places and seasons, the amount remains remarkably constant.

In volcanic regions, carbon dioxide may escape in considerable abundance through fissures in the earth, and may, on account of its relatively great density (it is one and a half times as heavy as air and twenty-two times as heavy as hydrogen), collect at the bottom of caves or valleys, as in the famous *Grotta del Cane*,<sup>1</sup> near Naples, and the Poison Valley of Java. The gas, also, may dissolve under pressure in underground water, from which it escapes with effervescence (as at Spa and Vichy in Europe, or at Saratoga Springs, New York), when the water rises to the surface as a spring.

Carbon dioxide, frequently spoken of as carbonic acid gas, was first identified by Joseph Black, in 1757, as a gas produced by the heating of chalk, and as a constituent of atmospheric air. It can very easily be obtained by acting on soda (sodium carbonate), chalk, limestone, marble (three varieties of calcium carbonate or carbonate of lime), or any other carbonate, with an acid. Usually one employs marble and hydrochloric acid, a convenient form of apparatus being shown in Fig. 33. Acid is poured through the funnel A, and acts on a quantity of marble placed in the bottle B. Gas is rapidly evolved and passes through the delivery tube C, to the bottom of a cylinder, from which it displaces the air. The reaction which takes place is represented by the equation:



<sup>1</sup> So called because in this cave the carbon dioxide collects to a depth of only two or three feet, so that while a man may enter the cave with impunity, a dog is suffocated by the gas.

It is interesting to note that the escape of carbon dioxide from the earth was known to Vitruvius, a Roman architect of the first century B.C., who speaks of currents of air "coming up in a pregnant state through porous fissures to the places where wells are being dug, and finding men engaged in digging there, stop up the breath of life of their nostrils by the natural strength of the exhalation." And he also mentions that as a safeguard against accidents, one should "let down a lighted lamp, and if it keeps on burning a man may make the descent without danger."

Large quantities of carbon dioxide are also produced industrially by the combustion of coke, coal and other carbonaceous fuels, as well as in various fermentation processes.

Carbon dioxide is a colourless gas which, as it is much heavier than air, can be poured from one vessel to another like water; and a soap bubble, blown with air, will float on a layer of carbon dioxide, like a cork on water. Carbon dioxide supports neither life nor combustion, and may be used to extinguish fire, as can be shown by pouring carbon dioxide into a beaker in which a candle is burning. This fact is made use of in the construction of a number of portable *fire extinguishers*, which are filled with a solution of sodium bicarbonate and contain also a bottle or glass tube containing sulphuric acid. By inverting the apparatus or by breaking the tube by means of a plunger, the acid is caused to mix with the solution of bicarbonate and carbon dioxide is formed. This dissolves in the solution, which is then ejected through a nozzle by the pressure of the excess of gas, and the water, assisted to some extent by the carbon dioxide which is set free, extinguishes the fire. The effectiveness of the arrangement can be increased by adding to the liquid in the extinguisher, glue, liquorice or some other material which is capable of forming a foam or froth.

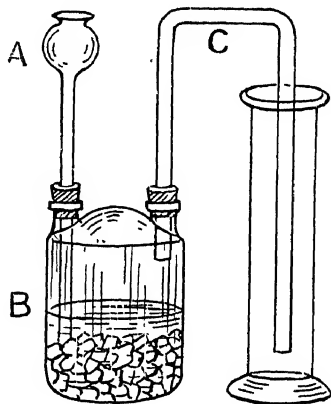
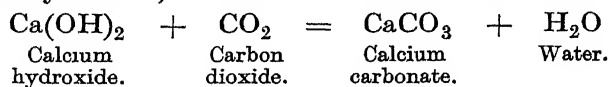


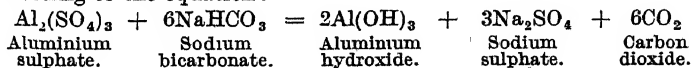
FIG. 33.—Preparation of carbon dioxide.

In the Foamite apparatus, aluminium sulphate and sodium bicarbonate are added to water, whereupon carbon dioxide and gelatinous alumina (aluminium hydroxide) are formed.<sup>1</sup> When the mixture is ejected from the apparatus, a stiff, stable foam containing carbon dioxide is produced which effectively "blankets" or smothers the fire.

When carbon dioxide is passed into lime water, a turbidity is produced owing to the fact that the gas reacts with the slaked lime (calcium hydroxide) and forms insoluble carbonate of lime, thus:



<sup>1</sup> According to the equation:



This reaction is used as a *test* for carbon dioxide.

Carbon dioxide can be liquefied comparatively easily, and the liquid is placed on the market in strong steel cylinders. At  $20^{\circ}\text{C}$ ., the vapour pressure amounts to 59 atmospheres. On allowing the liquid to be discharged through the nozzle of the cylinder into a cloth bag, rapid evaporation takes place and the temperature falls to such an extent that the liquid freezes to a snowlike solid. Since this solid sublimates or passes into gas, without melting, at  $-79^{\circ}\text{C}$ ., it is extensively employed as a refrigerant. Mercury, for example, which melts at  $-40^{\circ}\text{C}$ ., can readily be frozen to a hard solid by its means, and it is also employed in railway refrigerator cars used for the transport of ice-cream, fish and other food-stuffs. Blocks of compressed solid carbon dioxide are placed in wooden or cardboard containers on the floor of the car, and the heavy cold gas which is formed by sublimation gradually rises, filling the whole car and overflowing through vents at the top. Since the latent heat of sublimation is great, and since the solid block is well insulated by its gaseous envelope, sublimation takes place only slowly, and the amount of solid carbon dioxide required is therefore comparatively small. It has been found, indeed, that carbon dioxide snow, or "dry ice" as it is sometimes called, is as effective as more than ten times its weight of ice.

Carbon dioxide snow has also found application as a local anæsthetic and for cauterising warts, etc.

At the ordinary temperature and pressure, water dissolves nearly its own volume of carbon dioxide. At other pressures, the amount dissolved is approximately proportional to the pressure, in accordance with what is known as *Henry's law*. Soda water and other natural or manufactured aerated waters and effervescent beverages, contain carbon dioxide dissolved under pressure. The use of carbon dioxide for the preparation of aerated waters was first introduced by Priestley.

Since oxygen is being removed and carbon dioxide is continually being poured into the air in large quantities, not only in regions of volcanic activity but everywhere, owing to the respiration of animals, the combustion of coal and other carbonaceous fuels, processes of fermentation and other industrial operations; and since, as we have seen, the composition of the air remains remarkably constant, the questions very naturally arise: How does nature maintain the balance between oxygen and carbon dioxide? How does she achieve the degree of constancy in the composition of the air which is so remarkable?

An important part of the answer to these questions was given



by the qualitative experiments of Priestley and the later quantitative experiments of NICOLAS THÉODORE DE SAUSSURE (1767–1845), early in the nineteenth century; for these experiments showed that the green leaves of plants take up carbon dioxide and water from the air, and that, through the radiant energy of sunlight and in presence of the chlorophyll or green colouring matter in the leaves, the carbon dioxide and water vapour are used to build up, step by step, various complex compounds such as sugar, starch and cellulose. During the process, there is set free and given up to the air a quantity of oxygen equal in volume to the carbon dioxide removed. Thereby, the air is sweetened and purified and made more suitable for the support of animal life.

While the green vegetation on the earth's surface thus plays a very important part in maintaining the constancy of composition of the air, large quantities of carbon dioxide are also removed from the air by solution in rain and in the water of the rivers and oceans.

That **water vapour** is present in the air is made evident by the formation of clouds and mists when air is cooled, or by the fact that certain substances, *e.g.* calcium chloride, *deliquesce* or become moist when exposed to the air. The proportion of water vapour present in the air may, however, vary very greatly. Air is said to be saturated with moisture when the partial pressure of the water vapour in the air<sup>1</sup> is equal to the vapour pressure of water at the existing temperature. At 15° C., the vapour pressure of water is 12·7 mm. of mercury. When, therefore, the partial pressure of the water vapour in the air amounts to 12·7 mm. of mercury at 15°, the air will be saturated with moisture. If the total atmospheric pressure is 760 mm., the partial pressure of 12·7 mm. represents  $12\cdot7/760=0\cdot0167$  of the whole pressure; or, the partial pressure of water vapour in air saturated with moisture at 15°, is about 1·7 per cent. of the total pressure. Under these conditions, 100 volumes of air contain 1·7 volume of water vapour.

It is not, however, with the absolute amount of water vapour in the air, or in a given volume of the air, that we are primarily concerned, for it is not on this that our comfort depends. It is the *relative humidity* of the air that is of importance, or the amount of moisture present compared with the amount which would be present if the air were saturated. At 15° C. the air is saturated when the partial pressure of the water vapour is 12·7 mm. of mercury. The humidity is then 100 per cent. If

<sup>1</sup> Or the fraction of the total pressure which is due to the water vapour.

the partial pressure is only 6.35 mm., the humidity is 50 per cent. We have, however, already seen that evaporation of moisture from the surface of the skin is nature's chief means of regulating the temperature of the body, or of preventing the temperature from rising too high; and bodily comfort depends on a continued, moderate rate of evaporation. If the air surrounding the body is saturated with water vapour, or if the humidity is 100 per cent., then evaporation of water from the surface of the skin will be prevented. The air, we say, is moist—although really it is the body that is moist. If, on the other hand, the relative humidity of the air is low, whatever the absolute amount of moisture may be, evaporation takes place from the surface of the body, and the air is said to be dry.

It has now become more fully recognised that the feeling of "stiffness" in a crowded or badly ventilated room is due not to increase in the proportion of carbon dioxide in the air but to deficient evaporation of moisture from the surface of the body. It can be largely overcome by keeping the air in motion. The currents of air produced by means of fans or by the use of open fire-places remove the humid air which is in contact with the skin and so promote evaporation. The air feels fresher. The supply of fresh air, the preservation of the proper degree of humidity, and the keeping of the air in motion so that the layer of moisture-laden air in contact with the skin is removed, are the requisites of good ventilation.

The **Rare Gases** of the atmosphere, under which name are included HELIUM, NEON, ARGON, KRYPTON and XENON, form a group of related elements the discovery of which forms one of the most romantic episodes in the history of chemistry. To understand this aright, we must go back to the time of Cavendish, one of the most eminent chemists of the eighteenth century.

The HON. HENRY CAVENDISH, a man noted for his great ability no less than for his extreme shyness and hatred of publicity, was the elder son of Lord Charles Cavendish and grandson of the Second Duke of Devonshire. Born at Nice in 1731, he was educated at Cambridge and devoted his life entirely to scientific investigations. In 1766 there was published his first scientific memoir, in which he showed that different kinds of air have different specific gravities. In 1781, Cavendish established the constancy of the composition of the air, and in 1784, he determined the composition of water. His investigations, both chemical and physical, covered a very extensive field and

placed him in the very front rank of eighteenth-century natural philosophers.

Insignificant in appearance and accustomed to wear the costume of a former generation, Cavendish was shy and awkward with strangers, and shunned the society of his fellow men. He had a "singular love of solitariness," and, solitary and alone, he passed, in 1810, into the Great Beyond.

In 1785, desiring to study more fully the properties of nitrogen (then called "phlogisticated air"), with the object, more



HENRY CAVENDISH.

especially, of deciding "whether there are not in reality many different substances confounded together by us under the name of phlogisticated air," Cavendish carried out experiments which are not only at the very root of the discovery of the rare gases but which, in the early years of the present century, were developed into an industrial process for the production of nitric acid from the air. Repeating experiments first carried out by Priestley, Cavendish showed that when electric sparks are passed through air, combination of nitrogen and oxygen takes place; and if a

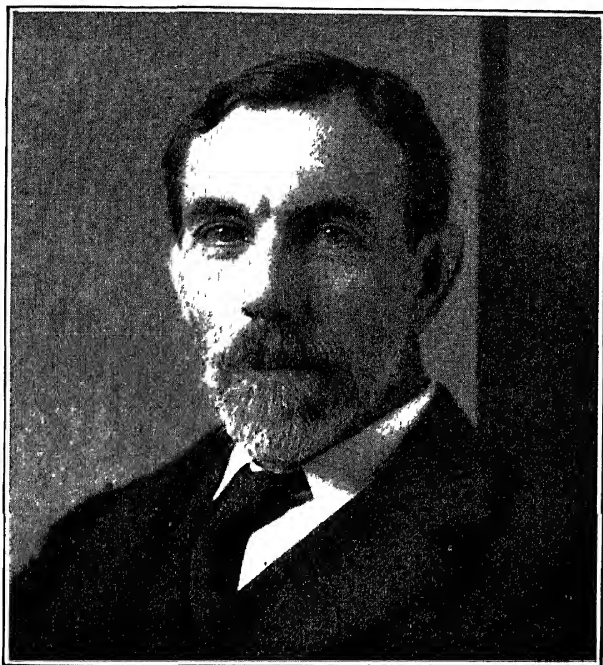
solution of potash is present in the vessel of air, nitre or saltpetre is formed. By adding further quantities of oxygen and continuing to pass the sparks, the nitrogen could be entirely removed, and any excess of oxygen remaining could be absorbed by a solution of *liver of sulphur* (potassium sulphide). As a result of his experiments, Cavendish found that no matter how long the passage of electric sparks was continued, there always remained a small bubble of gas, the volume of which was "certainly not more than  $\frac{1}{120}$  of the bulk of the phlogisticated air [nitrogen], let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, . . . we may safely conclude that it is not more than  $\frac{1}{120}$  part of the whole."

Little dreaming that in that bubble of gas five hitherto unknown elements were contained, Cavendish pushed the investigation no farther, for the apparatus (the spectroscope) which would have enabled him to do so, had not yet been invented; and for over a hundred years, the importance of Cavendish's experiment was overlooked, and the little bubble of gas, so big with scientific interest, was ignored. Until 1893, therefore, chemists everywhere believed that dry air, freed from incidental impurities, consisted solely of oxygen and nitrogen, together with small amounts of carbon dioxide; and so confident were they that they knew all about the composition of the atmosphere that the announcement of the discovery of a new element in the air, made by the late LORD RAYLEIGH and SIR WILLIAM RAMSAY at a meeting of the British Association held at Oxford in 1894, was received with surprise and incredulity. The story of that discovery is one which is full of interest to all students of science, for it is the story of skilful and accurate experiment and of clear and logical reasoning.

**Discovery of Argon.**—The late Lord Rayleigh, while engaged in the accurate investigation of the density of different gases, found that "atmospheric nitrogen," or the gas left after removal of the oxygen from the air, had a somewhat greater density than nitrogen obtained from one of its compounds. The difference was not great, being only about 1 part in 230, but it was much greater than the possible errors of the determination, for these amounted only to about 1 part in 10,000. Various hypotheses were put forward by Rayleigh to account for the discrepancies, but none of them stood the test of experiment. Lord Rayleigh announced the results of his density determinations early in 1893, and invited the help of chemists in explaining the divergent results. No answer, however, to this invitation

was forthcoming until, early in 1894, William Ramsay, at that time Professor of Chemistry at University College, London, asked and received permission to carry out experiments on atmospheric nitrogen, with the view of explaining its anomalous behaviour.

WILLIAM RAMSAY, the only child of his parents, was born at Glasgow in 1852. After completing his courses of study at the Universities of Glasgow, Heidelberg and Tübingen, Ramsay



WILLIAM RAMSAY.

occupied a junior post in the Chemistry Department of the University of Glasgow till 1880, when he became Professor of Chemistry at University College, Bristol. In 1887, Ramsay was called to fill the Chair of Chemistry at University College, London; and there he remained till his retirement in 1912. It was at University College, London, that his epoch-making researches were carried out

A "precocious dreamy youth," as he characterised himself, Ramsay developed into the most brilliant of British chemists since the time of Sir Humphry Davy; and through his great

scientific achievements, more especially through his discovery of a whole missing group of elements in the periodic system of Mendeléeff, he won from Governments, Universities and Scientific Academies, honours and distinctions such as are bestowed on few. In 1902, he was created a Knight Commander of the Order of the Bath, and in 1904, he was awarded the Nobel Prize for Chemistry. Lovable and sociable, musical and having the gift of tongues, Ramsay possessed personal qualities which endeared him to all; but illness came, and after months of suffering, his eager and ardent life came to an end in July 1916.

Making use of the fact that nitrogen combines with magnesium to form a nitride, Ramsay passed "atmospheric nitrogen" repeatedly over red-hot magnesium and obtained a small quantity of residual gas which did not combine with the metal. At the same time, Lord Rayleigh repeated the experiment of Cavendish, but on a much larger scale, and instead of a small bubble he obtained no less than two litres<sup>1</sup> of gas which did not combine with oxygen.

In carrying out this experiment, Lord Rayleigh made use of the apparatus shown in Fig. 34.<sup>2</sup> Through the stopper closing

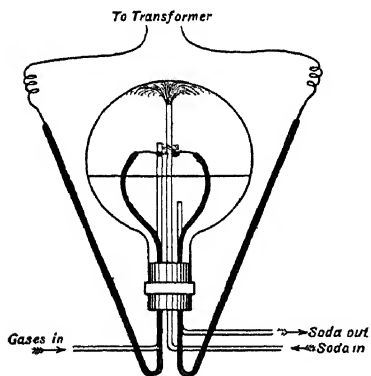


FIG. 34.—Preparation of argon.

the mouth of a large glass balloon there pass two thick copper wires with stout platinum terminals, between which an arc discharge is caused to take place. A mixture of air and oxygen, in such proportions that all the nitrogen combines with oxygen when heated by the electric discharge, is passed in through a tube, and a solution of caustic soda is kept circulating through the flask. This solution removes the oxides of nitrogen which are formed, and at the same time serves to keep the flask cool.

The density of the residual gas obtained by Ramsay and by Lord Rayleigh was found to be about 20, compared with the value 14 for nitrogen. The gas was subjected to chemical and physical treatment of every imaginable kind, but it underwent no change; and attempts to cause it to combine with other substances were equally unsuccessful. It was a quite inactive

<sup>1</sup> A litre or 1000 cubic centimetres (c.c.) is equal to 1.76 pints. (See Appendix III.)

<sup>2</sup> Various improved forms of the apparatus were later employed.

and inert element, the first such element to be discovered, and it received, in consequence, the name *argon*.<sup>1</sup>

Argon, which forms rather less than 1 per cent. of air by volume, is a gas which is without colour, taste or smell. Until recently, it was of purely scientific interest, but it is now obtained commercially in large quantities from liquid air, and finds an important industrial application in filling incandescent electric lamps of the "half-watt" type. Owing to the presence of the gas, the tungsten filament of the lamp can be heated to a much higher temperature, and a brighter light can therefore be obtained, without dispersion of the metal and blackening of the bulb taking place.

On the basis of theory and experiment which cannot be more fully discussed here, the conclusion has been drawn that the molecule of argon is the same as the atom; the molecule is monatomic. The molecular weight has, therefore, the same value as the atomic weight, 39.9.

**Spectroscopic Identification of the Rare Gases.**—Since argon and the other rare gases are all chemically inactive, they cannot be distinguished from one another by chemical but only by physical means. For this purpose use is made of the *spectroscope*.

Light is regarded as consisting of ethereal vibrations, and light of a definite colour is produced by vibrations of a definite

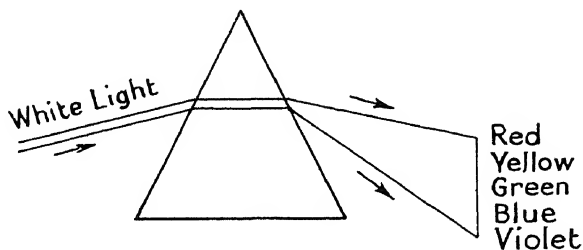


FIG. 35.—Formation of a spectrum.

wave length. White light is composed of vibrations of every wave length, within certain limits, and when such light is caused to pass through a prism of glass, the rays of light of different wave length are refracted or bent to a varying extent—the shorter waves being refracted more than the longer (Fig. 35). A narrow beam of white light, therefore, on passing through a prism, is drawn out into a rainbow band, the colours of which merge continuously one into the other. This band of colours is

<sup>1</sup> From the Greek  $\alpha$  (alpha), not, and  $\epsilon\rho\gamma\omega\nu$  (ergon), work.

known as a *spectrum*. At one end the band is red, due to vibrations of long wave length, while at the other end, the band is violet, due to vibrations of short wave length. Between these two extremes we have orange, yellow, green, blue and indigo.

If a solid substance is gradually heated to incandescence, and if the light emitted is examined by means of a spectroscope

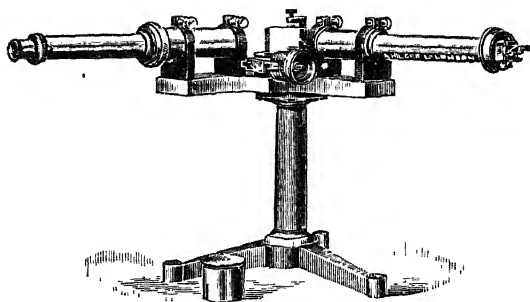


FIG. 36.—Spectroscope.

Light enters through a slit in the end of the right-hand tube, and after passing through the glass prism is observed by means of the telescope on the left.

descent, yields a *continuous* spectrum.

When, however, a gas is made incandescent, by passing an electric discharge, for example, through the gas contained in a tube under reduced pressure (called a Plucker tube or Geissler tube), it is found that the spectrum no longer consists of a continuous band of colour, but of isolated lines, each line occupying a certain definite position and corresponding with light of a

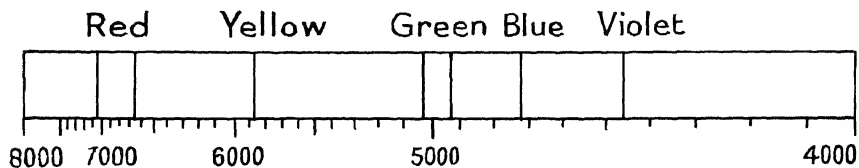


FIG. 37.—Spectrum of helium.

The scale is in ten-millionths of a millimetre.

certain definite wave-length (Fig. 37). Since each gas gives its own characteristic spectrum or arrangement of lines, it is easy, by determining the position of the lines, with the aid of a spectroscope, to identify a gas. It was by means of their spectra that the different rare gases were identified and distinguished; and the spectroscope was also the means whereby, at an earlier



period (1861), ROBERT WILHELM BUNSEN (1811–1899), Professor of Chemistry, and GUSTAV ROBERT KIRCHHOFF (1824–1887), Professor of Physics in the University of Heidelberg, discovered the elements cæsium and rubidium.

**Helium.**—In 1868, the French astronomer, Professor Janssen, and the English astronomer, Sir Norman Lockyer, while examining the spectrum of the sun's photosphere during an eclipse, observed a yellow line which they could not find in the spectrum of any known terrestrial substance. Lockyer concluded that it must therefore be due to some extra-terrestrial element to which he gave the name of helium.<sup>1</sup> The element remained unknown on the earth until the year 1895, the year after the discovery of argon, when it was isolated by Ramsay from the uranium-containing mineral, cleveite. That a gas was given off by this mineral on treatment with acid was already known, but the gas was thought to be nitrogen. On examining its spectrum, however, Ramsay at once saw that the gas was neither nitrogen nor argon; and on sending a specimen of the gas, which had provisionally been named krypton, to the late Sir William Crookes for spectroscopic examination, he received in reply a telegram, "Krypton is helium." In other words, the gas which Ramsay had obtained from the mineral cleveite was none other than the helium of Janssen and Lockyer.

Investigation of this new gas showed that it is an element with the atomic weight 4.00, and that, like argon, it is chemically inert and incapable of forming any compounds. As in the case of argon, also, the molecule contains only one atom. It is the most difficult of all gases to liquefy, and it was not till 1908 that it was obtained in the liquid state by Kammerlingh Onnes of Leyden. It boils, under atmospheric pressure, at a temperature of  $-268.7^{\circ}\text{C.}$ , and by evaporating liquid helium under reduced pressure, a temperature of  $0.8^{\circ}\text{A.}$  can be produced. In 1926, it was obtained in the solid state.

Helium is now known as a disintegration product of radioactive substances, and it is consequently found in most radioactive minerals. It has also been found in certain naturally occurring waters, *e.g.* in the mineral springs of Bath, and it occurs in air to the extent of about 5 parts per million. The main source from which it is obtained is the natural gas which escapes from the earth in certain districts of Canada and of America, more especially in the province of Ontario and the States of Texas, Oklahoma, Colorado and Kansas; and in recent years large quantities of helium have been isolated from natural gas

<sup>1</sup> From the Greek *ἥλιος* (*hēlios*), the sun.

for use in filling airships.<sup>1</sup> For this purpose it possesses the great advantage over hydrogen of not being inflammable. Although the density of helium is twice as great as that of hydrogen, its lifting power is not much less; for the lifting power depends on the difference between the density of the gas and the density of air. Taking the densities of hydrogen, helium and air as 1, 2 and 14.4 respectively, the lifting powers of hydrogen and of helium will be as 13.4 is to 12.4. That is to say, the lifting power of helium is 92.5 per cent. of the lifting power of hydrogen.

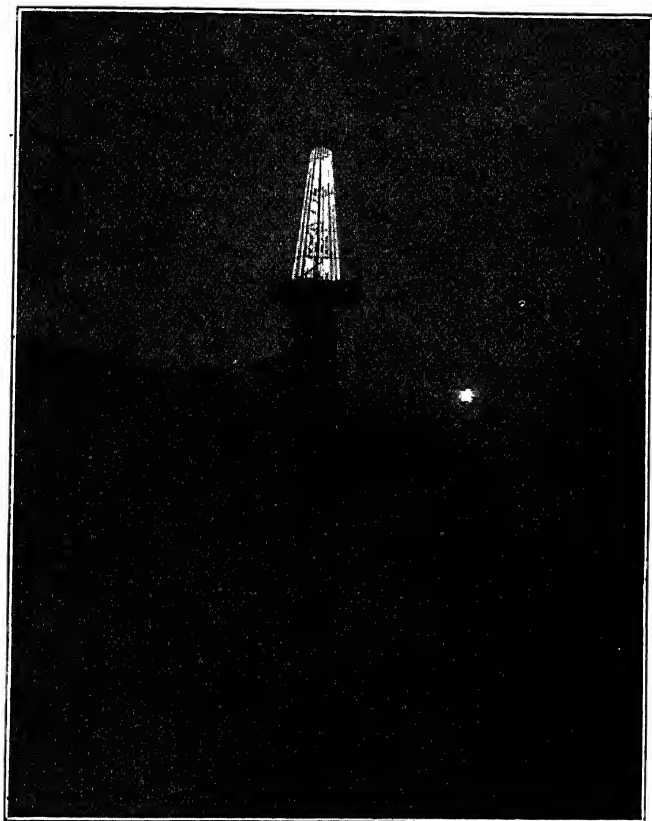
**Neon, Krypton, Xenon and Radon.**—With the discovery of the monatomic elements, argon and helium, which are chemically inert and may therefore be regarded as having a valency of nought, a new group, a group with zero valency, had to be inserted in the Mendeléeff classification of the elements. Since, moreover, helium preceded the positive univalent element lithium, and argon the element potassium, it seemed probable that other similar elements of zero valency should exist which would, in their turn, fall into place in front of the other positive univalent elements. In 1896, therefore, a systematic search for the missing elements was commenced by Ramsay and Travers, who carried out a prolonged and most careful fractionation of liquid air; and their investigation was pursued with such energy and ability that in a short time three new elements were obtained from the air, namely, *neon*, *krypton* and *xenon*.<sup>2</sup> The identity of these gases was established by means of the characteristic spectra which they give; and the determination of their atomic weights showed that they were the elements sought for. In the space of a few years, therefore, no fewer than five new elements, present in the air, were discovered; and the series of the rare gases was completed some years later by the discovery of niton, or, as it is now usually called, *radon*, the radioactive gas or “emanation” given off by radium.

Besides helium and argon, neon, which occurs in the air to the extent of only 15 parts per million, has already found practical application, and is used as a filling for “Osgilim” lamps and neon tubes, used for testing the sparking plugs of motor cars and in the construction of illuminated signs. Under the influence of the electric discharge, the gas glows with a brilliant flame colour, and since the light emitted has a great power of penetrating mist and fog, neon lamps are now being used for lighthouses at air-ports.

<sup>1</sup> Six million cubic feet of helium were extracted in the United States in 1928.

<sup>2</sup> From the Greek νέος (neos), new; κρυπτός (kryptos), hidden; and ένος (enos), strange.

The discovery and isolation of five hitherto unknown elements is one of the great epics in the history of scientific investigation ; and no one who lived through the eventful years 1895-1898, when the discovery, in rapid succession, of gas after gas, new element after new element, was announced to the scientific world, could



Neon Lighthouse.

(From *The Approach towards a System of Imperial Air Communications*, by permission of the Controller of H.M. Stationery Office )

fail to feel a thrill such as Keats felt when, for the first time, he read Chapman's translation of *Homer* :

Then felt I like some watcher of the skies  
When a new planet swims into his ken ;  
Or like stout Cortez when with eagle eyes  
He stared at the Pacific—and all his men  
Look'd at each other with a wild surmise—  
Silent, upon a peak in Darien.

## CHAPTER XI

### THE PRODUCTION OF FIRE

THE manner in which the first visible combustion, or fire, was brought about on the earth, will doubtless always remain unknown. It may, perhaps, have had its origin in some lightning flash, or in the sparks struck from the flints of primitive man; or it may have been produced by the self-heating of combustible material, or by the rubbing together of dried wood; or it may be that, as in the *Song of Hiawatha* :

Gitche Manito, the mighty,  
Breathed upon the neighbouring forest,  
Made its great boughs chafe together,  
Till in flame they burst and kindled.

But in whatever way fire was first produced, its importance and value were early recognised, as we can understand from the sanctity with which all primitive peoples have endowed the hearth; from the legend of Prometheus who “searched out the source of fire . . . which has shown itself a teacher of every art to mortals and a great resource”; as well as from the later belief of the followers of Zoroaster, that fire is the special abode of divinity.

And even at the present time, we are not likely to underrate the importance of combustion when we remember that our present-day civilisation, in all its manifold forms of expression, in manufactures, in railway and steamship transport, in artificial illumination, etc., is based mainly on a process of combustion.

**Ignition Point.**—We have, it is true, already learned that combustion in air is a chemical reaction between the combustible substance and the oxygen of the air, but we have still to enquire how this reaction is initiated. Clearly, something more than mere contact is required, for we know that coal gas can be allowed to escape from the burner, or a candle or piece of wood or coal may be left exposed to the air, or even to pure oxygen, without any sign of fire

In order that a combustible material shall not only undergo

combustion, but shall continue to burn with production of light, it is necessary to heat the material up to a certain temperature, known as its *ignition point*. Combustion then goes on of itself. The explanation of this fact is that the velocity or vigour of every chemical change is increased by elevation of the temperature. At the ordinary temperature, the oxidation of the candle or the coal takes place so slowly that no change is apparent even over long periods of time. If, however, the temperature of the combustible material is raised, the rate at which it reacts with the oxygen of the air rapidly increases, and consequently the production of heat which accompanies the reaction also rapidly increases until, at a certain point—the ignition point—the reaction takes place with such rapidity that the heat which is produced by the process of oxidation is sufficient to raise the substances to incandescence and also to maintain the burning substance at a temperature above the ignition point. The process of combustion is thus enabled to proceed continuously.

On the other hand, if the burning substance is cooled sufficiently, the temperature is lowered to below the ignition point, and combustion ceases. A simple experiment will serve to demonstrate this important truth. If a piece of metal wire gauze is held at a distance of half an inch or an inch above a burner from which coal gas is issuing, and if a light be applied to the gas *above the gauze*, it will be found that the flame of burning gas is arrested by the gauze and does not pass through to the burner (Fig. 38); for the wire gauze conducts the heat

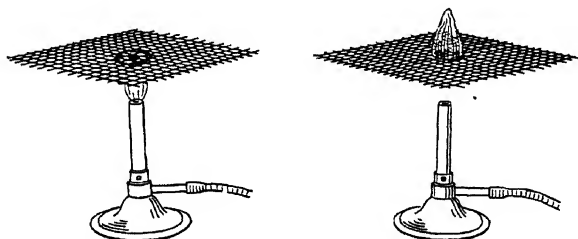


FIG. 38 —Extinction of flame by wire gauze.

of the flame away so rapidly that the temperature is lowered to below the ignition point of the gas. Only after the gauze has become quite hot does the gas below the gauze become ignited. Similarly, if the gauze is brought down on a flame of burning gas, the flame is extinguished at the gauze. The gas itself, however, passes through, as can be shown by bringing a light to the upper surface of the gauze, when the gas will take fire.

The cooling power of wire gauze received, early last century,

an application of the highest importance in the miner's safety lamp invented by SIR HUMPHRY DAVY (1778-1829), of whose life a short account will be given at a later point. This lamp has undergone a striking change and marked improvement since the time of its first invention, and the modern safety lamp (Fig. 39)

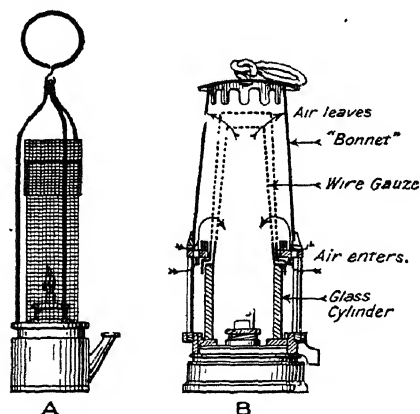


FIG. 39.—Miner's safety lamp.

In the old form of lamp, A, the flame was surrounded by a closed cylinder of wire gauze which considerably diminished the light emitted by the lamp; but in the modern type, B, a cylinder of glass is inserted, whereby the efficiency of the lamp is greatly increased.

shows little sign of the means whereby safety is secured. But on careful examination it is seen that all the holes through which air can pass to the flame, or the hot air and products of combustion can pass out, are protected by fine wire gauze. Although, therefore, the combustible gas, the "fire-damp," can pass through this gauze and can burn inside the lamp, the flame cannot pass through the gauze and be communicated to the explosive mixture of fire-damp and air in the mine.

Warning of the presence of the dangerous fire-damp is given to the miner through the luminous flame of the lamp becoming crowned by a "cap" of pale blue flame. The greater

the amount of fire-damp the larger is the cap.

**Slow Combustion.**—The process of combination with oxygen which, as we have seen, is the essential feature of the combustion process in air, may, however, go on appreciably even at temperatures below the ignition point. Thus, when fine iron filings are sprinkled over the surface of a wet test tube and the tube inverted over water, the iron slowly combines with the oxygen of the air and the water rises in the tube. In this experiment we have a demonstration of the familiar fact that iron, when exposed to moist air, *rusts*. Rust is an oxide of iron ( $\text{Fe}_2\text{O}_3$ ), and the process of rusting is therefore a process of oxidation, a process of combustion, against which it is necessary to protect, by paint or other means, all iron structures exposed to the air, if we would have them last. The rusting of iron is said to be a process of *slow combustion*, because the temperature does not rise to the point of incandescence. Slow combustion can be demonstrated more strikingly with the metal aluminium which combines with

oxygen more vigorously than iron does. When exposed to the air at the ordinary temperature, aluminium remains apparently unchanged. As a matter of fact it rapidly combines with the oxygen of the air, but the coherent invisible film of oxide which is formed on the surface, protects the metal from further attack, and therefore no change is apparent. By coating the surface of the metal with mercury, however, a liquid amalgam or alloy of mercury and aluminium is produced, and the formation of a coherent film of aluminium oxide is thereby prevented. The aluminium is consequently no longer protected from the continued action of the oxygen of the air. In this case it is observed that the aluminium undergoes oxidation quite rapidly, the oxide forming a moss-like growth on the surface of the metal. The heat which is produced by the oxidation, although quite marked, is dissipated so quickly that the temperature does not rise to the point of incandescence, and so no light is seen.

Processes of slow combustion, or combustion unaccompanied by the emission of light, are going on continually within our bodies, and are the source of the heat by which the temperature of the body necessary for health is maintained. When air is drawn into the lungs, the oxygen passes or diffuses through the thin walls of the blood vessels and combines with the hæmoglobin present in the red blood corpuscles. On the other hand, carbon dioxide passes from the venous blood into the air-spaces of the lungs and is expelled in the expired air. The oxygen, in the form of oxy-hæmoglobin, is carried by the blood to all parts of the body, and oxidises or burns the lactic acid and other carbonaceous materials contained in the cells and tissues of the body. Carbon dioxide and water are thereby produced, and the former is conveyed by the venous blood back to the lungs and so got rid of.

The presence of carbon dioxide in expired air is readily shown by blowing through a tube into clear lime water (a solution of slaked lime or calcium hydroxide in water). The liquid very speedily becomes turbid owing to the separation of insoluble carbonate of lime, formed by the combination of carbon dioxide with the slaked lime (see p. 155).

In the processes of putrefaction and decay, also, we have examples of slow combustion, in which animal and vegetable material is oxidised by the oxygen of the air with the co-operation of various micro-organisms; and efficient aeration, as in a rushing and tumbling stream, is an excellent means of purifying water from all kinds of organic and harmful contamination.

**Spontaneous Combustion.**—Under favourable conditions,

slow combustion may pass into rapid combustion with production of light. For, if the heat which is produced by the combination of the oxygen with the combustible material is prevented from being dissipated, the temperature will go on rising gradually; and as the temperature rises, the vigour of the combustion or chemical combination increases. More and more heat, therefore, is produced in a given time, the temperature rises more and more rapidly until, finally, it reaches the ignition point of the combustible material. The slow combustion passes into rapid combustion, and the combustible material takes fire without the application of external heat; in other words, it undergoes *spontaneous combustion*. In this way arise, for example, the so-called "gob" fires, in spaces from which coal has been removed, and where coal-dust and fine coal remain behind; so also may fire break out in coal bunkers and in other confined spaces in which combustible matter, like oily cotton waste, is stored without proper ventilation. Such spontaneous combustion will, of course, take place with special ease in the case of readily inflammable substances, or substances which have a low ignition point, such as phosphorus. Thus, if this substance is dissolved in the liquid known as carbon disulphide (a compound of carbon and sulphur), and if the solution is then poured on a sheet of filter-paper, or thin blotting-paper, the carbon disulphide soon evaporates and leaves the phosphorus on the paper in a finely divided state. The oxygen of the air rapidly unites with the phosphorus, and the heat which is thereby developed soon raises the temperature to the comparatively low ignition point of the phosphorus, and rapid combustion sets in.

Although the most familiar examples of combustion are those which take place in air, the term combustion must not be restricted to such cases. Combustion, in its widest meaning, is a process of chemical action in which so much heat is generated that the burning substance becomes incandescent and emits light; and such a process may occur even when no air or oxygen is present. Thus, for example, the gas hydrogen will burn not only in air, with production of the substance water ( $\text{H}_2\text{O}$ ), but it will also burn in the gas chlorine with formation of the compound known as hydrogen chloride ( $\text{HCl}$ ), or hydrochloric acid gas. And similarly, other cases of combustion are known which do not depend on the presence of oxygen, and are not processes of oxidation.

From the preceding discussion of combustion in which it has been emphasised that combustion is, in its essence, a process of chemical reaction, it will be readily understood that the terms



combustible and supporter of combustion are, in the case of gases at least, reciprocal terms. Hydrogen and coal gas (which is really a mixture of gases) are said to be combustible, and oxygen is said to be a supporter of combustion simply because our atmosphere contains free oxygen, whereas hydrogen and coal gas have to be made artificially and introduced into the air, through a tube or jet, for example. If, however, the atmosphere consisted of or contained not oxygen but hydrogen and if oxygen had to be made artificially, one would then say that hydrogen is a supporter of combustion and oxygen a combustible gas, for the oxygen gas could then be burned from a jet in an atmosphere of hydrogen.

In Fig. 40 is shown a glass lamp chimney closed at the bottom by means of a cork. Through this cork there pass the tube, A, connected with a supply of coal gas, and the tube, B, which is open to the air. The upper end of the lamp chimney is closed by an asbestos or metal plate pierced by a hole about 1 cm. in diameter. When desired, this hole can be closed by means of a plate.

Having closed the hole in the upper plate, the gas is turned on. This fills the glass cylinder and escapes through the tube B, at the end of which it may be ignited. If the hole in the upper plate be now opened, the coal gas will pass through and may be ignited. At the same time, owing to the draught produced the flame which was burning at the exterior end of tube B will pass along the tube and will come to rest at the *interior* end of the tube, this flame being fed by *air* drawn in through the tube B. There are now two flames: one, at the top of the cylinder, which is due, as one would say, to coal gas burning in air, and the other, inside the cylinder, at the end of the tube B, which, we must say, is due to air (oxygen) burning in coal gas.

Even when the combustion is due to the combination of the combustible material with oxygen, to a process of oxidation as we have called it, the oxygen need not be present in the gaseous form, but may be yielded up by some compound containing it. Various well-known substances, such as chlorate of potash

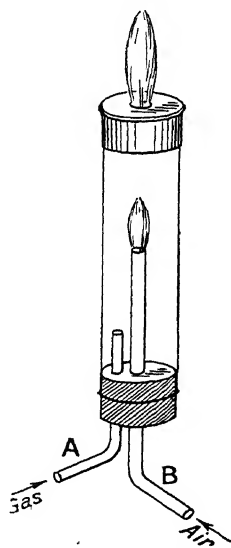


FIG. 40.—Coal gas burning in air, and air in coal gas.

( $\text{KClO}_3$ ) and saltpetre or potassium nitrate ( $\text{KNO}_3$ ), can act as suppliers of oxygen in this way, and the use of such substances for promoting combustion has long been known. *Touchpaper*, for example, the slowly burning paper which is so familiar in connection with fireworks, is prepared by soaking paper in a solution of saltpetre, and allowing it to dry. The saltpetre is in this way deposited in the fibres of the paper and renders the latter more readily combustible. Such paper does not require the presence of gaseous oxygen for its combustion, but will burn in an atmosphere of nitrogen or other inert gas. In the case of gunpowder, also, as has already been pointed out, saltpetre is similarly made use of as a reservoir of oxygen.

**Production of Fire.**—In order to bring about the rapid combustion which we call fire, it is necessary, as we have seen, to raise the temperature of some combustible material to a certain point, the ignition point. Nowadays this raises no difficulty; and it may be regarded as not the least of the services which chemistry has rendered to man, that it has put it within his power to obtain fire at will, with a minimum both of trouble and expense. From the primitive method of rubbing two dried sticks together to the use of the flint and steel, and from the latter to the modern safety-match, is indeed an advance the importance of which for our modern civilisation it would be difficult to estimate and impossible to over-estimate.

One of the characteristics of chemical action, as we have seen it exemplified in the process of combustion, is the production of heat, but it was not till early in the nineteenth century that practical suggestions were made for the employment of such means of producing fire. One of the earliest of these suggestions which had a certain measure of success was made about 1810 by a Frenchman named CHANCEL, who tipped strips of wood with a mixture of potassium chlorate and sugar, bound together by means of gum. When this composition is dipped into concentrated sulphuric acid (oil of vitriol), the very powerful oxidising agent chloric acid is set free. In contact with this acid the sugar is oxidised so vigorously that it takes fire; and this combustion is then communicated to the wood splint. Small cases with a set of matches and a bottle of sulphuric acid were sold under the names of "Instantaneous Light Box" and Hertner's Eupyrion.

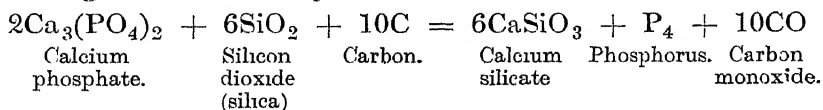
Late in 1826 or early in 1827, JOHN WALKER, an apothecary of Stockton-on-Tees, in England, invented a match the tip of which consisted of a mixture of potassium chlorate and sulphide of antimony, and this mixture could be ignited by being drawn

between folds of glass paper. These matches, known as "friction-lights" and later as lucifers, were the first friction matches used.

Although the "friction lights" were a great improvement on the flint and tinder then in use, they were soon superseded by another match in which use was made of the readily inflammable substance phosphorus.

**Phosphorus**,<sup>1</sup> a non-metallic element, was discovered in 1669 by HENNIG BRAND, an impoverished merchant of Hamburg, who, searching for the philosopher's stone (as the story goes) with a view to retrieving his fortunes, heated to a high temperature, along with sand, the residue left on the evaporation of urine.<sup>2</sup> He did not, it is true, succeed in the chief object of his quest, but he obtained instead a substance which on account of the brilliance with which it glowed in the dark was called *phosphorus mirabilis*. It was exhibited at various Courts of Europe as one of the marvels of the time.

At the present time, phosphorus is produced industrially by heating to a high temperature in an electric furnace (Fig. 41), a mixture of calcium phosphate, silica (sand) and coke, when the following reaction takes place:



The phosphorus vapour is condensed under water. When purified, phosphorus forms a white wax-like solid (for which reason it is called white phosphorus) which, as we have learned, glows in the dark owing to its combination with the oxygen of the air. It has a low melting-point (44° C.), and takes fire when

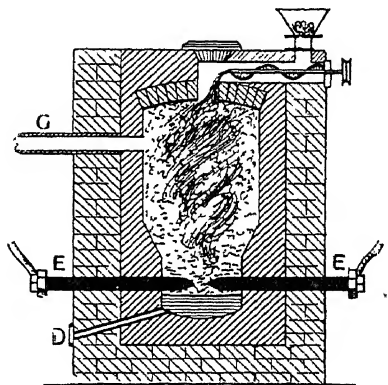


FIG. 41.—Electric furnace for the production of phosphorus (diagrammatic).

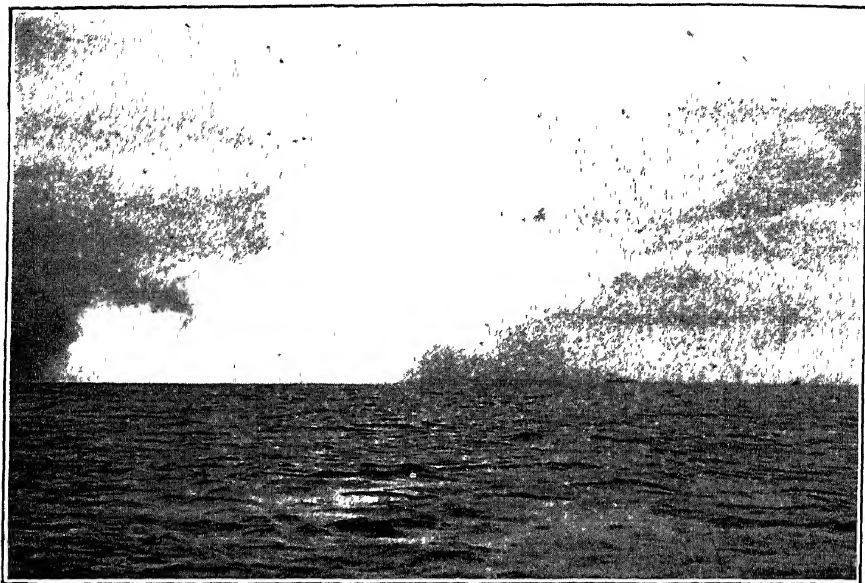
The reaction mixture is fed in at the top of the furnace and is heated to a high temperature by the electric arc formed between the electrodes EE. Phosphorus vapour escapes through G and slag is run off through D.

<sup>1</sup> From  $\omega\varsigma$  (phōs), light, and  $\phi\acute{\epsilon}\rho\epsilon\iota\nu$  (pherein), to bear.

<sup>2</sup> This residue contains a compound of phosphorus known as sodium hydrogen ammonium phosphate,  $\text{NaNH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$ . It was called *microcosmic salt* by the alchemists because it occurs in what was regarded as an extract of the human microcosm.

heated in the air to about  $35^{\circ}$ . It burns vigorously in air or oxygen, forming, as has been pointed out, phosphorus pentoxide ( $P_2O_5$ ). In moist air this oxide combines with water and forms droplets of an acid known as phosphoric acid. A dense cloud is thereby produced which settles only very slowly. For this reason, burning phosphorus was occasionally used for producing smoke screens in the Great War.

Phosphorus is very poisonous, and inhalation of its vapour causes "phossy-jaw," or necrosis of the bones of the jaw.



Phosphorus smoke screen produced by a bomb dropped from an aeroplane.

In 1830, CHARLES SAURIA, a French chemistry student at Dôle, in the Jura, conceived the idea of incorporating in the composition used for matches, a small quantity of (white) phosphorus, which, on account of its ready inflammability, seemed particularly suitable as a fire producer.<sup>1</sup> In 1832, this idea was successfully applied and phosphorus-tipped matches, known as Congreves, were very widely used until the end of the nineteenth century. The tips of these matches consisted, essentially, of a

<sup>1</sup> Even as early as 1786 an Italian had brought out in Paris "le briquet phosphorique," which consisted of a bottle coated internally with phosphorus, and matches tipped with sulphur. When one of the matches was rubbed against the inside of the bottle so as to remove a little of the phosphorus and was then brought into the air, the phosphorus took fire. Such a match was used by Faraday as late as 1827.

mixture of phosphorus and some substance rich in oxygen, such as potassium chlorate, or red lead (oxide of lead), bound together with gum or glue, and coloured with various pigments. The accidental fires, however, due to the ready inflammability of the phosphorus, and the general danger of its unrestricted use; the number of deaths, accidental or intentional, produced by phosphorus poisoning; and the terrible disease known as "phossy-jaw," which attacked the workers in the match factories, led to a ban being placed on what had been hailed as a boon; and the use of ordinary white or yellow<sup>1</sup> phosphorus has, in all civilised countries, been forbidden by law.

The element phosphorus, however, exists not only in the readily inflammable and poisonous white variety, but also in a totally distinct form, that of a dark red crystalline powder—*red phosphorus*—which is insoluble in carbon disulphide. Such physically distinct forms of an element are frequently spoken of as *allotropic*<sup>2</sup> *modifications*.

Since this red phosphorus, which is produced by heating white phosphorus in a closed vessel to a temperature of 240° C., is much less readily inflammable than white phosphorus and is also non-poisonous, attempts were made to utilise it for the manufacture of matches. Difficulties were at first encountered, but these were ultimately overcome; and the first so-called Swedish or safety match was manufactured in Sweden in 1855. In these matches the red phosphorus is not incorporated in the match head, but is used in the composition with which the rubbing surface is coated. The match tip consists of a mixture of sulphide of antimony ( $\text{Sb}_2\text{S}_3$ ) and an oxidising substance such as potassium chlorate, red lead ( $\text{Pb}_3\text{O}_4$ ) or potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ); and sulphur and charcoal are sometimes added. This mixture will not take fire when rubbed on a rough surface, but only when rubbed on the specially prepared surface which is coated with a paste of red phosphorus mixed, sometimes, with sulphide of antimony and powdered glass. Moreover, in order to diminish the risk of accidental fire through the glowing wood of a used match, safety matches are soaked in a solution of alum, sodium phosphate, ammonium phosphate, or some other salt. The charred wood of the match is thereby strengthened, and the match ceases to glow almost immediately after being blown out.

When the use of white phosphorus was forbidden, the attention of chemists was directed to the discovery of other materials

<sup>1</sup> When exposed to sunlight, white phosphorus slowly becomes yellow or even red in colour owing to its conversion into the so-called red phosphorus.

<sup>2</sup> From *ἄλλος* (allos), other, and *τρόπος* (tropos), mode.

which might be used instead, and a non-poisonous match was produced which possessed the advantage of the old phosphorus match, of striking on any rough substance. In the case of this "strike anywhere" match, the tipping composition consists of a mixture of sulphide of phosphorus ( $P_4S_3$ ) and potassium chlorate, or other oxidising material, bound together with glue, and powdered glass is also sometimes added to increase the friction and so facilitate the inflammation of the match head.

To render the wood of the match more readily inflammable and so allow of the combustion passing on from the tip to the wood, the latter is impregnated with paraffin wax, although, sometimes, sulphur is employed instead.

## CHAPTER XII

### MATTER AND ENERGY

**Forms of Energy.**—In considering the process of combustion in air, attention was directed mainly to the materials involved, the oxygen, carbon, sulphur, etc., and to the products of the reaction, such as carbon dioxide and sulphur dioxide. The definition of combustion, however, as a chemical change accompanied by the emission of heat and light, clearly indicates that there is another aspect of the process to which consideration must be given. Heat and light are forms of *energy*, and energy may be defined as work or the capacity for doing work. Combustion, therefore, must be considered not merely as a process whereby matter is transformed but as a process in which energy is set free; a process which can be utilised for the performance of work. In the combustion of ordinary fuels, indeed, this aspect of the process is the most important.

When wood or coal is burned in the domestic fire, or under a boiler for the production of steam, it is not the chemical nature of the fuel or of the products of combustion which are really of interest, but the amount of energy in the form of heat which is liberated in the process of combustion. Similarly, when petrol (gasoline) is purchased for use in the engine of a motor-car, one is really buying so much energy, for it is the amount of energy which can be obtained from a gallon of the fuel which is of importance.

We see, then, that just as a reservoir of water at the top of a hill represents so much *potential energy* which, when the sluice gates are opened, becomes converted into *kinetic energy* or energy of motion which can then drive a turbine and become converted into mechanical energy; so combustible substances, together with the oxygen of the air, represent so much potential energy, and the process of combustion is like the downward rush of the waterfall in being a process by which the potential energy becomes available for doing work. It is, then, in their power of liberating energy and of doing work that we see the real value of combustibles.

Although the association of energy with chemical change is made very obvious to us in connection with the process of combustion, it is also found in connection with all chemical changes. Every chemical system, every collection of substances which can spontaneously undergo chemical change, represents a certain amount of potential energy, and the material change which we observe, and which constitutes what we call a chemical reaction, is merely the outward sign of the conversion of so much potential energy (chemical energy) into other forms of energy—heat energy, light energy, electrical energy or some other form of energy. It is, moreover, mainly by learning how better to employ energy and how better to effect its transformation into different forms, that man has progressed towards a higher and more complex civilisation, and if one would grasp the spirit of modern chemistry and appreciate its importance in man's ascent from a state of primitive barbarism, one must learn to regard a chemical change not merely as involving some material transformation, but as representing a flow of energy out of or into the substances undergoing change.

**Conservation of Energy.**—Just as there exists a law of conservation of mass so there is a LAW OF CONSERVATION OF ENERGY. The sum total of energy is constant and can neither be increased nor diminished—it can only be altered in form. Mechanical energy, for example, can be converted, through friction or rubbing, into heat energy; and in this way primitive man obtained fire. Mechanical energy, also, can be converted into electrical energy, through the medium of the dynamo; and chemical energy is converted into electrical energy in the voltaic cell. In each case, a definite amount of one form of energy is equivalent to a definite amount of another form of energy. Thus, the work which is done when a weight of 2000 grams (2 kilograms) falls through a distance of 21·3 cm., or when the weight of 1 pound falls through a distance of 3·08 feet, would, if it were completely converted into heat energy, give rise to 1 calorie, an amount of heat which would raise the temperature of 1 gram of water by 1° C. Since the work done by a falling body is measured by the product of weight multiplied by the vertical height of fall, it will be clear from the preceding statement that 42,600 ( $2000 \times 21\cdot3$ ) gram-centimetres or 3·08 foot-pounds of mechanical energy are equivalent to 1 calorie of heat energy.

**Heat of Reaction.**—Although in the process of combustion, heat is evolved, it must not be thought that all chemical change is accompanied by an *evolution* of heat. In some cases, the initial substances possess less energy than the final products, and the



chemical change therefore takes place with *absorption* of heat. Energy, that is to say, must be supplied to the initial substances in order that they may pass into the final products of change. We distinguish, therefore, between *exothermal* reactions or reactions accompanied by evolution of heat, and *endothermal* reactions or reactions accompanied by absorption or taking in of heat energy.

From the law of conservation of energy it follows that the change in energy which accompanies a chemical change or transformation of matter is, for a given weight of the reacting substances and under specified conditions, constant and definite in amount. When this energy is in the form of heat energy, it is spoken of as the *heat of reaction*, and its value is positive or negative according as the reaction is accompanied by evolution or absorption of heat.

When carbon (*e.g.* charcoal) is burned in air or in oxygen so as to form carbon dioxide, 96,700 calories of heat energy are liberated for every gram-atomic weight<sup>1</sup> (12 grams) of carbon burned: and this fact is represented by writing the equation for the process (*cf.* p. 153) in the form:



The heat evolved, 96,700 cal., is called the *heat of combustion* of carbon (in the form of charcoal), or the heat of formation of carbon dioxide, and is the amount of heat liberated when 1 gram-molecule (44 grams) of carbon dioxide is formed by the combustion of carbon.

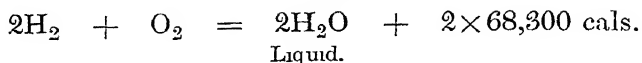
The equation for the combustion of carbon shows (*cf.* p. 63<sup>x</sup>) that 12 grams (1 gram-atom) of carbon require, for complete combustion, 32 grams (1 gram-molecule) of oxygen, or 22.4 litres of oxygen at N.T.P. Since the ratio of nitrogen to oxygen in the air, by weight, is as 77 : 23, or as 3.35 : 1, it follows that for every 32 grams of oxygen there must be 107.2 grams of nitrogen. The weight of *air* required for the complete combustion of 12 grams of carbon is, therefore, 139.2 grams. Moreover, since the ratio of nitrogen to oxygen, by volume, is as 79 : 21, or as 3.76 : 1, the volume of air, at N.T.P., required for the complete combustion of 12 grams of carbon, will be  $22.4 + 84.2 = 106.6$  litres.

If one employs, as is usually done in technical practice, the pound as unit of weight and the cubic foot as unit of volume, the appropriate calculation shows that 12 lbs. of carbon require,

<sup>1</sup> The atomic weight expressed in grams.

for complete combustion, 378.3 cubic feet<sup>1</sup> of oxygen, or 378.3 + 1422 = 1800.3 cubic feet of air, at 60° F., and under a pressure of 30 inches of mercury.

For the combustion of hydrogen, we have the equation :



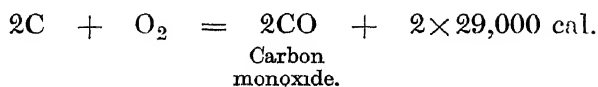
That is to say, when 2 grams of hydrogen are burned in air or in oxygen so as to form 18 grams (1 gram-molecule) of water, and when the water vapour formed is condensed to the liquid state, 68,300 cal. are evolved. This is the heat of combustion of hydrogen.

If the water vapour is not condensed to the liquid state, the heat of combustion will be less than 68,300 cal. by 9700 cal., which is the latent heat given out by 18 grams of steam on condensing to water.

As in the case of carbon, one can calculate the weight and volume of oxygen or of air required for the combustion of a given amount of hydrogen, and one finds that for the combustion of 2 grams of hydrogen (occupying a volume of 22.4 litres at N.T.P.), there are required 16 grams of oxygen, or 11.2 litres of oxygen at N.T.P. When burned in air, 2 grams of hydrogen will require 69.6 grams of air, or 53.3 litres of air at N.T.P.

Further, 2 lbs. of hydrogen (occupying a volume of 378.3 cubic feet at 60° F. and under a pressure of 30 inches of mercury) will require for combustion, 189.2 cubic feet of oxygen, or 900.2 cubic feet of air at 60° F. and under a pressure of 30 inches of mercury.

**Carbon Monoxide.**—When carbon is burned in a deficient supply of air, there is formed not carbon dioxide but a very different gas known as *carbon monoxide*, the combustion taking place in accordance with the equation :

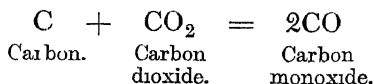


That is to say, for every 12 grams of carbon burned, only 29,000 cal. of heat are liberated in place of the 96,700 cal. obtained when the carbon burns in an abundant supply of air.

*Carbon monoxide*, which was first obtained in the eighteenth century by heating oxides of metals with charcoal and which is produced in large quantities at the present day in many

<sup>1</sup> The molecular weight of a gas expressed in pounds (e.g. 32 pounds of oxygen), occupies a volume of 378.3 cubic feet at 60° F. and under a pressure of 30 inches of mercury.

metallurgical operations, can readily be obtained by passing carbon dioxide through a tube in which charcoal or carbon is heated to a bright red heat. At this high temperature, the carbon combines with part of the oxygen of the carbon dioxide, as shown by the equation :



The production of carbon monoxide is frequently observed in a brightly glowing coal fire. The coal lying at the bottom of the grate unites with the oxygen of the incoming air to form carbon dioxide ; and this gas, passing up through the glowing mass of coal (carbon) is *reduced*,<sup>1</sup> as it is said, to carbon monoxide. The carbon monoxide is an inflammable gas and burns with a blue flame at the top of the glowing mass of coal.

Carbon monoxide differs from the dioxide not only in being a combustible gas but also in being intensely poisonous. This is due to the fact that the gas combines with the hæmoglobin of the blood to form a very stable, bright-red compound, carboxy-hæmoglobin, so that the hæmoglobin is no longer able to take up oxygen from the air entering the lungs and to carry it to the different tissues of the body. The presence of even 1 volume of carbon monoxide in 5000–10,000 volumes of air will cause headache and produce symptoms of poisoning, while if 1 per cent. of carbon monoxide is present, unconsciousness and death will occur in a few minutes. Many cases of poisoning by carbon monoxide have occurred owing to its presence in illuminating gas, and in the products of imperfect combustion in stoves or in the engines of motor-cars, from which it passes out in the exhaust.<sup>2</sup> In cases of necessity, however, one may protect oneself from harm by wearing a gas mask in which the air containing carbon monoxide is drawn over a mixture of the oxides of manganese, copper, cobalt and silver—a mixture known technically as *hopcalite*. On passing over this mixture, the carbon monoxide is oxidised to carbon dioxide by the atmospheric oxygen.

When carbon monoxide is burned, heat is evolved in accordance with the equation :



**Allotropic Forms of Carbon.**—To regard a substance, as

<sup>1</sup> The term *reduction*, which is the converse of oxidation, is applied to a process whereby the proportion of oxygen in a compound is decreased.

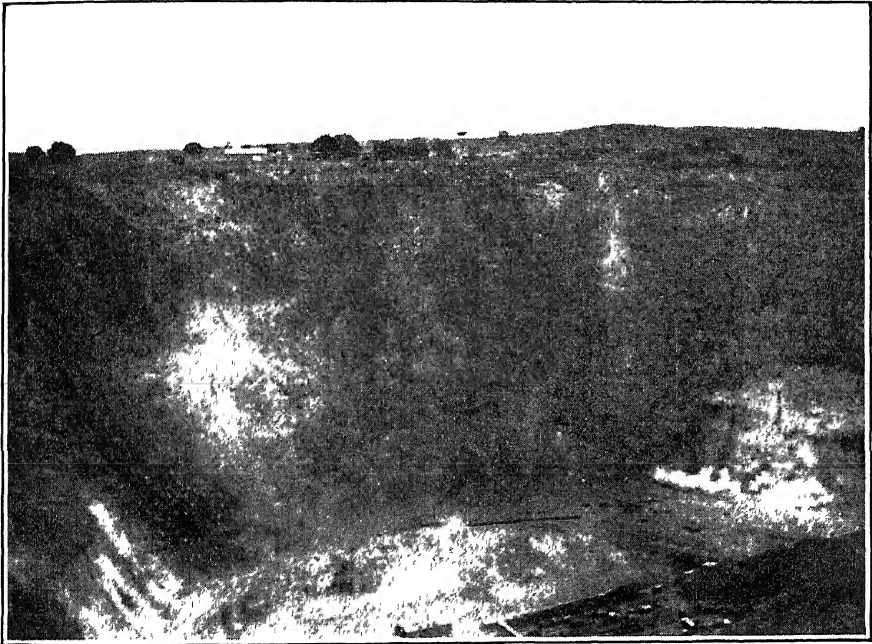
<sup>2</sup> Owing to the presence of carbon monoxide (5–9 per cent.) in the exhaust gases of a motor car, the unwisdom of running the engine in a closed garage will be obvious.

has been done in the preceding pages, as the vehicle of so much energy, and a chemical change as the outward and visible sign of energy change, is at once very instructive and suggestive; for it is clear that if one could make a substance take up energy—if one could, as it were, pump energy into a substance—one would thereby alter the amount of energy of which that substance is the carrier, and so change its properties. Such changes can, as a matter of fact, be brought about, and not a few elements are known to exist in so-called *allotropic* forms or modifications (p. 177), which differ from one another in containing or being the carriers of different amounts of energy.

The most familiar and longest known example of allotropy is found in the element carbon, which occurs naturally in the two different crystalline varieties, diamond and graphite. That these two physically different materials are chemically identical, is shown by the fact not only that they each yield carbon dioxide on being burned in oxygen, but that from equal weights of the allotropes equal weights of carbon dioxide are produced. Besides those two crystalline allotropes of carbon there are a number of so-called amorphous varieties of carbon, *e.g.* wood charcoal, animal charcoal, lampblack (soot), coke, etc. These materials, however, which are formed by the decomposition by heat of complex compounds, are not, perhaps, all pure carbon but contain probably other elements (*e.g.* hydrogen) in small and varying amounts. That this amorphous carbon and the two crystalline forms of the element are associated with different amounts of energy is made clear by the fact that the heats of combustion are different. Thus, 1 gram of diamond, graphite and amorphous carbon yield, when burned completely to carbon dioxide, 7873, 7832 and 8060 calories respectively. Charcoal (amorphous carbon), therefore, contains the largest, and graphite the smallest, amount of energy, and these are, respectively, the least and the most stable forms of carbon. The difference in energy content is probably associated with a difference in the arrangement of the electrons within the atom and in the arrangement of the atoms in the crystalline structure.

**Diamond.**—Diamond, the purest naturally occurring form of carbon and “the most valuable of gems, known only to kings” (as Pliny wrote of it), was introduced into Europe from India where, even at an early period, it had been found in various alluvial deposits. These deposits, over which legend and myth, such as Sinbad’s tale of the “Valley of Diamonds,” have cast a glamour, were almost the only source of diamonds until about 1725, when the diamond mines of Brazil were opened up. One

day, in 1867, however, children amusing themselves on the bank of the Orange River in South Africa, picked up a pebble of special brilliancy which was passed, somewhat carelessly, from hand to hand until it reached an expert, who recognised it to be a diamond worth £500. Soon after, other diamonds were discovered in the alluvial deposits of the Orange and Vaal Rivers, but the importance of these deposits was overshadowed in 1870-71 by the discovery of great diamond "pipes" at what later became Kimberley and at various places in its neighbourhood. These "pipes," which may, perhaps, be the necks of

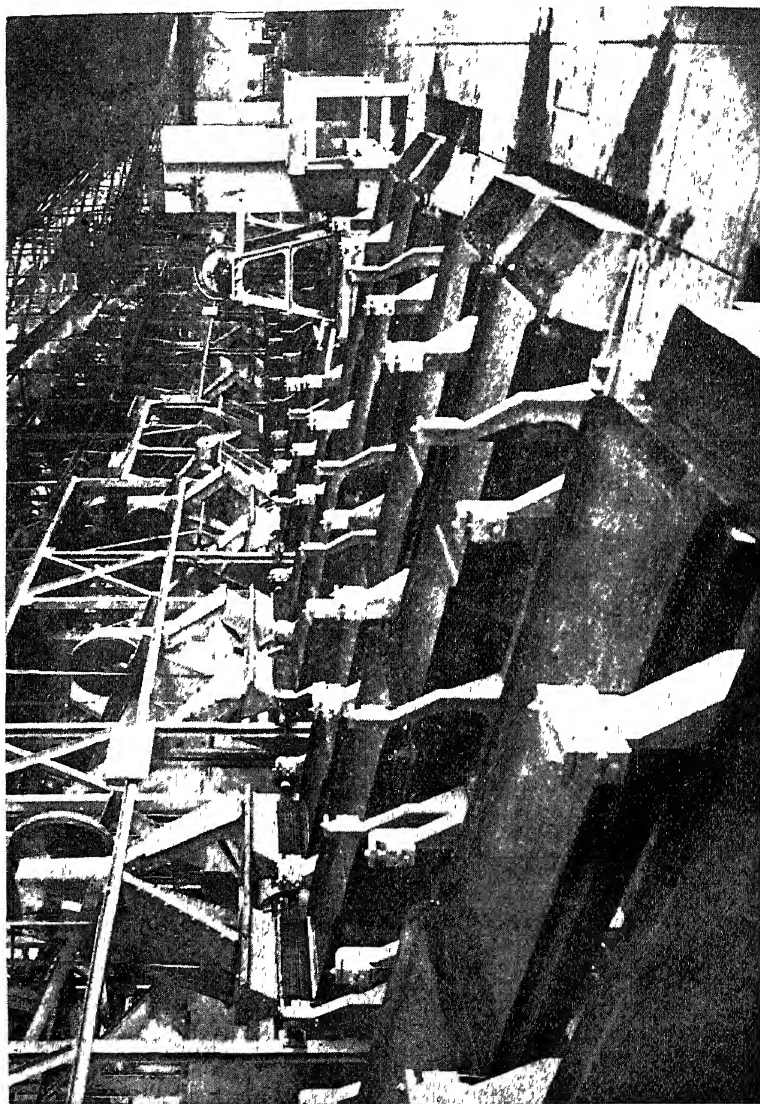


Firing a blast at the Premier Diamond Mine.

extinct volcanoes, extend vertically downwards to some unknown depth, and are filled with a heterogeneous rocky mass, known as "blue ground," in which the diamonds are embedded. Originally worked from the top, these pipes of blue ground are now mined by means of tunnels and galleries run in at different levels from a main shaft.

By far the largest deposits of diamonds are found, however, at the *Premier Mine* near Pretoria, in the Transvaal, which was opened only in 1903. In this enormous "pipe," having an area of over 370,000 square yards, and constituting the largest diamond

mine in the world, the great Cullinan diamond (called after the founder of the company) was found in January 1905. This



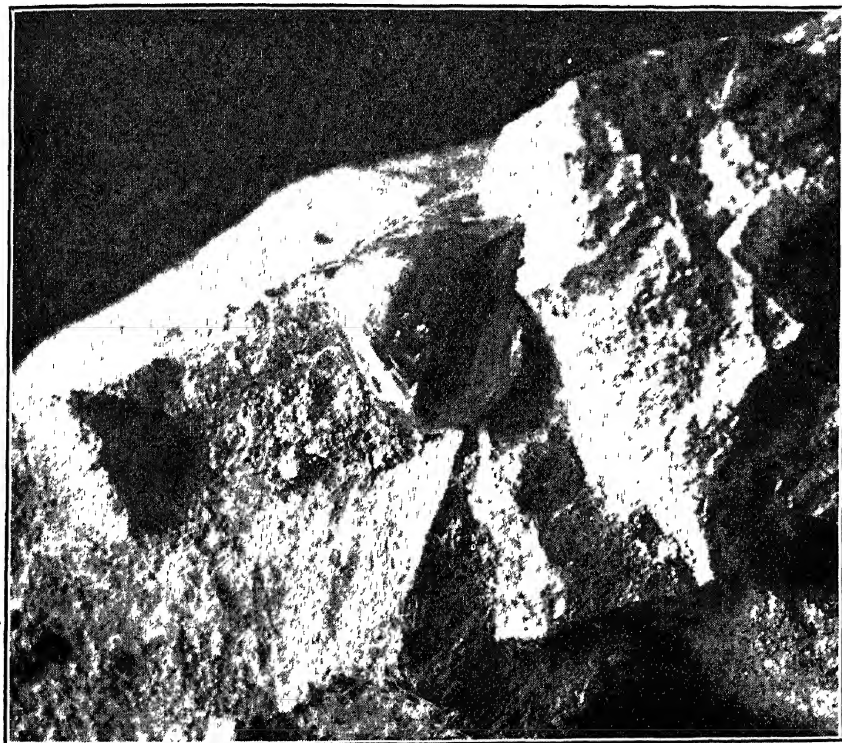
(Courtesy de Beers Consolidated Mines, Ltd.)  
Grease plates for retaining diamonds.

stone, which weighed nearly 3026 carats<sup>1</sup> (1.37 lbs. avoirdupois), was presented by the Transvaal Government to King Edward VII.

<sup>1</sup> The term *carat* is derived from carob bean formerly used, as a unit of weight, by diamond merchants in India. Its value is now fixed internationally at 200 milligrams.

It was cut into a number of stones, and the largest two of these (weighing 516·5 and 309 carats respectively)—the largest brilliants in existence—are among the Crown Jewels of Great Britain.

Not only from the mines but also from alluvial deposits worked, more especially, at Lichtenburg in the Transvaal and near Port Nolloth in Namaqualand, diamonds are obtained



(Courtesy de Beers Consolidated Mines, Ltd.)  
Diamond crystal in blue ground.

in considerable quantity, so that South Africa now supplies upwards of 90 per cent. of the total world production of diamonds.

In order to obtain the diamonds from the "blue ground" in which they are embedded, the latter is crushed and shaken with water, so as to set free the diamonds and wash away the lighter earthy matter. The "concentrates," consisting of diamonds and other minerals, are then carried by means of a regulated stream of water over large plates coated with grease. The

diamonds sink through the water and are caught in the grease, because the surface attraction between diamond and grease is greater than between diamond and water. The other minerals (garnets, etc.) are carried along in the stream of water.

Diamonds occur in single crystals, generally in the form of octahedra. For the most part, they are colourless and transparent, but some are of a pale yellow, blue or green colour. The index of refraction of light is high, and for this reason the diamond, when suitably cut and polished, strongly refracts and scatters the light, and so scintillates and flashes in varied colours. The diamond is the hardest of all naturally occurring substances,<sup>1</sup> and is, in consequence, used as a cutting, drilling and polishing material. For this purpose, the impure black diamonds, known as *carbonado* or *bort*, are largely employed. When heated to a high temperature out of contact with the air, diamond is converted into graphite.

**Graphite.**—Graphite, which is frequently also called black-lead or plumbago, on account of the fact that at one time it was confused with certain black ores of lead, occurs naturally in greyish-black, lustrous masses more especially in Ceylon (where the largest amount of graphite is mined), and in Madagascar. Deposits are also found in Bohemia, Siberia, America and elsewhere. It crystallises in plate-shaped crystals which readily slide over one another, so that graphite has a greasy or unctuous feel and is largely used as a lubricant. Unlike diamond, graphite is soft and readily marks paper,<sup>2</sup> and for this reason it has been employed, from the middle of the sixteenth century at least, for the manufacture of lead pencils. For this purpose, the graphite is now ground to a fine powder, washed with water to remove impurities and mixed with varying quantities of clay or powdered retort carbon, in order to produce pencils of different "hardness." The graphite paste is "squirted" through a die so as to form rods, and is then fired.

On account of its great resistance to heat<sup>3</sup> and the slowness with which it reacts with the oxygen of the air, graphite, mixed with a little clay, is largely used in the manufacture of crucibles; and as it is also a good conductor of electricity, it is used in the construction of dry cells and as electrodes in electro-chemical processes.

Graphite is now manufactured artificially in large quantity,

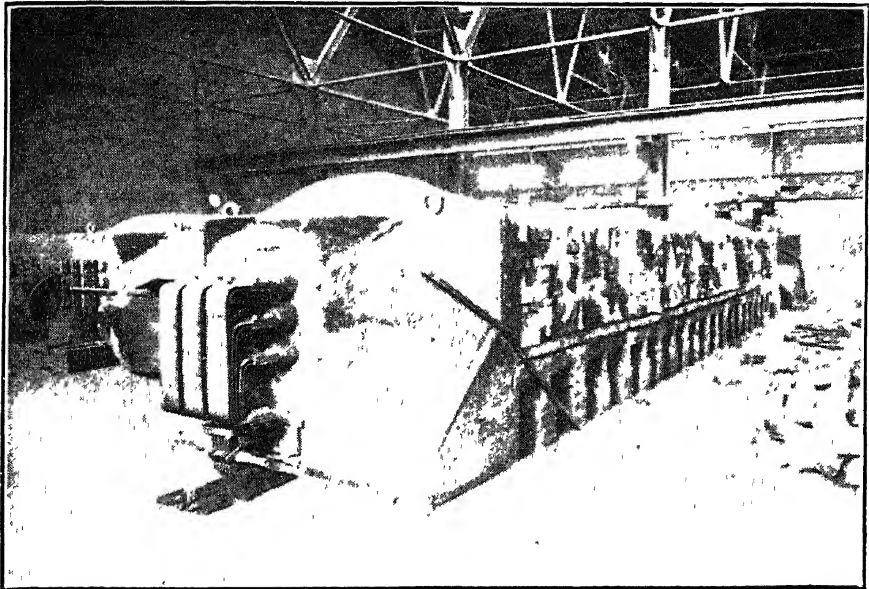
<sup>1</sup> The word diamond is a corruption of the Latin word *adamas* (Greek *ἀδάμας*), meaning invincible, and was applied to a very hard metal or mineral.

<sup>2</sup> The name graphite is derived from the Greek verb *γράφειν* (*graphein*), to write.

<sup>3</sup> Graphite melts only at a temperature of about 3500° C.



more especially at Niagara Falls, by a process due to the American chemist, EDWARD G. ACHESON. For the production of Acheson graphite, amorphous carbon (anthracite, coke, etc.), mixed with a small amount of oxide of iron, alumina or silica, and made into a stiff paste with tar, is heated to about  $3000^{\circ}\text{C}$ ., in an electric furnace, similar to that used for the manufacture of carborundum (see later). The silica and metal oxides added to the coke facilitate its conversion into graphite owing to the fact that compounds (known as *carbides*) are first formed and are then decomposed



(Courtesy Acheson Graphite Corporation )  
Graphite furnace in action.

at the high temperature of the furnace, the carbon being deposited as graphite.

The artificial graphite is superior to the natural mineral by reason of its greater purity and uniformity. In the diamond crystal, we have seen, the atoms of carbon are arranged in hexagonal formation, but the carbon atoms in the different layers do not lie in one plane: The layers are "puckered," as one can see on examining the model. In the case of graphite crystals, the same general arrangement of carbon atoms is found, but there are certain important differences in detail. In the case of graphite, the layers of carbon atoms are no longer puckered but are smoothed out to a plane and the distance between the layers

is greater than in the case of the diamond. For this reason graphite is softer than diamond and the layers move more easily over one another. To this is due the action of graphite as a lubricant.

**Charcoal and Lampblack.**—*Charcoal*, which is perhaps the most important of the so-called amorphous forms of carbon, is obtained by heating wood, bone, coconut shell, or other carbonaceous matter, in a closed vessel, or retort, out of contact with the air. When wood is so heated, volatile products—wood tar, water, wood spirit, acetic acid, acetone, and various gases—pass off and charcoal remains in the retort. This wood charcoal retains to some extent the structure of the wood, and the mineral matter originally present in the wood—potassium carbonate, calcium carbonate, silica—is also present.

Owing to the fact that charcoal possesses a very porous and foam-like structure, it exhibits, in a very high degree, the property of condensing on its surface or *adsorbing*, different gases and vapours;<sup>1</sup> and for this reason charcoal may be used for the removal of foul or noxious gases from the air. It found important application during the Great War in the construction of gas masks for protection against poison gas; and it is now largely used for removing gasoline vapour from the “natural gas” which escapes from many oil wells. The gasoline can be recovered by heating the charcoal.

The adsorptive power of charcoal is very greatly increased by lowering the temperature; and this fact is made use of for the purpose of producing high vacua. The tube or vessel to be evacuated is connected with a tube containing charcoal cooled by means of liquid air. Owing to the fact that helium is adsorbed to a very much less extent than other gases, a separation of this gas from the others can be effected.

Not only has charcoal the property of adsorbing gases, but it can similarly remove substances from solution. It is, therefore, frequently used for the removal of coloured impurities from liquids. A solution of litmus, for example, can be decolorised by shaking with charcoal; and this material is also used in sugar refining for the removal of the brown colouring matter from the crude syrup.

*Lampblack*, produced by the imperfect combustion of the residues left on the distillation of coal-tar, by burning natural gas against a cold metal or other suitable surface, and in other ways, is extensively used for the manufacture of printer's ink,

<sup>1</sup> It has been estimated that charcoal may expose a surface of 20,000 square yards, or about 4 acres, for 1 cubic inch of material.

India ink, and boot-blackening. In the rubber industry, also, lampblack finds a most important application, its incorporation into rubber giving to this material an increased toughness, elasticity and durability.

The element carbon occurs very widespread in nature, not only in the elementary state but also in the form of compounds. It is an essential constituent of all animal and vegetable matter, of carbon dioxide and the carbonates (*e.g.* limestone and dolomite), of petroleum and of coal; and the number of its compounds is so large that their study now constitutes a special branch of chemistry known as organic chemistry.

**Ozone.**—In the case of oxygen we have another example of an element existing in allotropic forms and associated with different amounts of energy.

Even at a very early time it was perceived—and of this Homer repeatedly makes mention—that the passage of lightning,

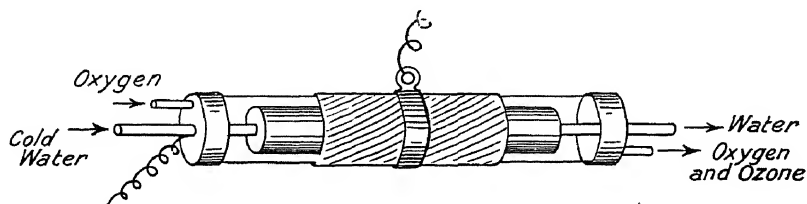


FIG 42.—Ozone apparatus.

The inner metal tube, through which water can be passed, is surrounded by a wider glass tube, coated on its outer surface with tin foil. Oxygen (or air) is passed through the wider tube. When the tin foil and the inner tube are connected with the secondary poles of an induction coil, a brush discharge takes place across the annular space which separates the two tubes.

or Jove's thunderbolts, was accompanied by a peculiar odour, likened to the fume of burning sulphur; and in 1785, the odour was observed still more distinctly by the Dutch physicist VAN MARUM, when a frictional electric machine was in operation. It was not, however, till 1840 that CHRISTIAN FRIEDRICH SCHÖNBEIN (1799–1868)—a Swabian by birth and Professor of Chemistry in the University of Basle from 1829 till his death—traced the cause of the *odeur électrique* to a definite gaseous substance to which he gave the name ozone.<sup>1</sup>

Ozone is produced when oxygen is passed through a space across which a brush discharge of electricity is taking place, as in the apparatus shown in Fig. 42. The oxygen takes up or absorbs some of the energy of the discharge and passes into the gas ozone, which betrays its presence by its characteristic odour.

<sup>1</sup> From the Greek *ὀζω* (*ozō*), I smell.

If the gas is passed through a tube immersed in liquid air, the ozone condenses to a deep blue coloured liquid, which readily undergoes explosive decomposition with formation of ordinary oxygen.

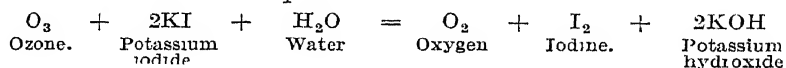
Since experiment has shown that ozone is formed from the element oxygen, and that when it decomposes it yields the element oxygen again, it is clear that the molecule of ozone must be built up of the same atoms as ordinary oxygen. It has, however, been found that whereas the molecular weight of oxygen is 32, the molecular weight of ozone is 48, or three times the atomic weight of oxygen. The molecule of ozone, therefore, must consist of three atoms of oxygen ( $O_3$ ), whereas the molecule of oxygen consists only of two ( $O_2$ ). The material change, therefore, or the chemical change which accompanies the absorption of energy, in the production of ozone, is the addition of a third atom of oxygen to the molecule of that gas.

The fact that the molecule of ozone is associated with more energy than the molecule of oxygen, is shown by the fact that when ozone passes into oxygen, heat is evolved in accordance with the equation :



Since ozone contains more energy than ordinary oxygen, it is a more active oxidising agent. It liberates iodine, for example, from a solution of potassium iodide,<sup>1</sup> and it tarnishes the surface of mercury. It destroys bacteria, and has therefore been used for the sterilisation of water ; and it is also used for bleaching flour, starch, waxes, etc.

<sup>1</sup> In accordance with the equation :



## CHAPTER XIII

### FUELS AND ILLUMINANTS

At the present day by far the greatest part of the energy necessary for the continuance of vital activity, as well as for carrying on the industrial life of the world, is derived from the energy of combustion of carbon and of its compounds. Through the oxidation of carbonaceous food by means of the oxygen taken in through the lungs, the vital activity of the animal organism is maintained; and the inert carbon dioxide which is produced is sent into the atmosphere in the expired air. The carbon contained in the carbon dioxide, however, does not thereby cease to be available, for the green plants, absorbing the radiant energy of sunlight, transform and utilise the carbon dioxide for the purpose of building up their own structures and producing compounds like starch and sugar, which again become the food and the source of energy in animals. In the case of the element carbon, which constitutes the basic element of all living matter, we find a continual circulation in nature, whereby the mutual preservation of the animal and vegetable worlds is secured. The green plants, as we see, act as transformers of the radiant energy of sunlight into the potential energy of combustible substances.

**Solid Fuels and Illuminants.**—Until comparatively recent times, down, say, to the sixteenth or seventeenth century, wood or wood charcoal was probably the almost universal fuel, industrial as well as domestic; but from the seventeenth century, from the time, in fact, when, in 1621, the English iron-master, DUD DUDLEY, introduced coal or coke in place of charcoal for the smelting of iron-ores, coal has become, in an ever-increasing degree, the immediate source of the energy on the utilisation and transformation of which our present-day civilisation depends, and it now occupies a position of unquestioned pre-eminence.

**Wood.**—In some of the great timber-producing countries, wood is still used to some extent as a fuel, although the increasing demand for timber, not only for constructional purposes, but also for use in many manufactures (of which the manufacture of paper may be taken as an example), makes the conservation of timber

supplies increasingly urgent. For domestic heating, undoubtedly, the cheerfully burning wood fire possesses many attractions, and when one thinks of the crackling wood and the dancing flames it is easy to understand the enthusiasm with which Robert Louis Stevenson, sheltering in the derelict blacksmith's forge at Silverado, on the slopes of Mount St. Helena, California, eulogised "that good creature—fire, which gives us warmth and light and companionable sounds, and colours up the emptiest building with better than frescoes."

It is, however, not with the cheerfulness with which the wood burns that we are concerned here, but with the important question of how much heat, how much energy it gives out on combustion; and when one considers the "calorific value" of wood, one finds it to be comparatively low, as shown by the number in the following table.

TABLE OF CALORIFIC VALUES.<sup>1</sup>

	Carbon.	Hydrogen.	Oxygen.	Calorific value B.T.U. per lb.
Cellulose ( $C_6H_{10}O_5$ ) <sub>n</sub>	44.5	6.2	49.3	7,500
Wood (dry) . . .	50.0	6.0	44.0	8,600
Peat (Irish) . . .	60.0	5.9	34.1	9,900
Lignite . . . .	67.0	5.2	27.8	11,700
Bituminous coal	88.4	5.6	6.0	14,950
Anthracite . . .	94.1	3.4	2.5	15,720

And the reason for this low value is not far to seek.

The combustible matter of wood consists, in the main, of the substance *cellulose*, which, as the numbers given in the table show, contains a large amount of oxygen. The compound may, therefore, be regarded as one which has already undergone extensive oxidation or extensive combustion. In fact, as the formula,  $C_6H_{10}O_5$ , indicates, hydrogen and oxygen are present in the compound in the same ratio as they are present in water, namely, two atoms of hydrogen to one atom of oxygen. We may, therefore, regard the hydrogen as completely oxidised or burned, and the heat of combustion of cellulose is, in consequence, equal (practically) only to the heat of combustion of the carbon present in it.

In the case of *dry* wood, in which the percentage of carbon is

<sup>1</sup> It must be noted that wood, peat and coal are not definite chemical compounds, and that the composition of the different kinds of coal may vary considerably. The numbers given in the table, therefore, are only approximate values representing, as it were, the composition and calorific value of an average member of the different classes.

higher than in cellulose, and in which other (resinous) substances of higher calorific value are present, the calorific value is higher than that of cellulose. It is, however, still rather low, and, under ordinary conditions, the calorific value is considerably less than that shown in the table, owing to the presence of from 15 to 20 per cent. of moisture. The value of wood as a fuel, therefore, is much less than that of coal which has a much higher heat of combustion.

*Coal.*—Coal, the nature and composition of which may vary very greatly, consists of the fossil remains of early, luxuriant vegetations—growing, decaying, accumulating, more especially in swampy districts, as in the Dismal Swamp of North Carolina and Virginia, where one can observe the formation of future coal-measures going on at the present day. Through an age-long process, the cellulose, of which the woody fibre essentially consists, is converted into more highly carbonised compounds, the proportion of hydrogen and oxygen becoming diminished owing to the formation of gaseous substances such as carbon dioxide and marsh gas. From the figures given in the above table, one can recognise the gradual carbonisation of cellulose, the materials peat, lignite or brown coal, bituminous coal and anthracite representing progressive stages in the natural process.

The process of carbonisation is accompanied by a diminution of the amount of gaseous and volatile matter which the fuel can yield on being heated, and this markedly affects the manner in which the different materials burn. Dry wood, as is known, burns readily and with a bright and cheerful flame, but anthracite, which represents the most advanced stage in the natural process of carbonisation of woody fibre, is ignited only with difficulty, and burns with a very small and not strongly luminous flame.

When one examines the different solid fuels from the point of view of their calorific value, it is found, as the figures in the last column of the table given above show, that with the progressive carbonisation, the heat-producing power of the fuel increases, so that among all the solid fuels, anthracite stands pre-eminent. A British thermal unit<sup>1</sup> represents the amount of heat required to raise the temperature of one pound of water through 1° F., and the numbers in the table show that whereas one pound of *dry* wood will give out, on burning, about 8600 units, an equal weight of bituminous or household coal will yield about 14,900, and anthracite will give 15,700 units. Since,

<sup>1</sup> Heat energy, as has been pointed out (p. 180), is very frequently measured also in calories, a calorie being the amount of heat required to raise 1 gram of water through 1° C. A British thermal unit is equal to 252 calories.

therefore, coal is purchased not for the sake of the material itself but for the energy which can be obtained from it, it is surely only rational that the price paid should be related to the heat-producing value of the coal. This is, in fact, the basis on which many large consumers of coal contract for their supplies.

During the past fifty or sixty years there has taken place throughout the world an enormous increase in industrial production, and the great river of energy which has thus flowed through the channels of industry, has had its source mainly in coal. The control and direction of such a flow of energy is a matter on which man may legitimately congratulate himself, but some anxiety cannot but be felt at the rate at which the great reservoir of energy is being depleted. The world's workable coal-supply, it has been estimated, amounts to some seven million million tons, and as this is being consumed at the rate of about fourteen hundred million tons a year, the coal reserves of the world will be exhausted in some five thousand years.

The depletion of their coal reserves is for some countries much more serious than for others, owing to the way in which the coal reserves are distributed throughout the different countries of the world. Thus, while the United States possess 51·8 per cent. of the world supply, Canada possesses only 16·4, China 13·5, Germany 5·7, and Great Britain 2·6 per cent. At the present rate of production, the coal reserves of the United States will last five thousand years; those of Great Britain less than one thousand years. The question, how most efficiently to utilise the irreplaceable coal reserves is, at the present day, exercising the minds of the scientific leaders of industry and is coming to be regarded, in most countries, as a matter of urgent national importance.

*The Distillation of Coal.*—Coal is not a definite chemical substance, but a complex mixture of substances, the nature of which is not yet definitely known. The essential elementary constituents of coal are, as we have seen, carbon, hydrogen and oxygen, but the elements nitrogen and sulphur also occur in small amounts. Since the composition of the different kinds of coal varies considerably, as shown by the table on p. 194, it will be readily understood that when coal is subjected to "destructive distillation" by being heated in retorts out of contact with air, the nature of the products as well as their relative amounts will depend on the kind of coal distilled. They depend, also, very markedly on the temperature at which the distillation is carried out.



When bituminous coal<sup>1</sup> is subjected to "destructive distillation," there are produced: (1) a combustible gas, used for heating and for illuminating purposes; (2) a watery liquor containing ammonia, derived from the nitrogen compounds contained in the coal; (3) a dark-coloured liquid, coal tar; (4) coke, which remains as a solid residue in the retorts. The nature of this solid residue depends on the temperature of distillation.

When the main object is to produce gas for heating and illumination, or hard coke for use as a fuel or in iron smelting and other metallurgical operations, the distillation is carried out at a temperature of about 1100° C. Under such conditions, one ton of dry coal yields about 11,500 cubic feet of gas, 25 lbs. of sulphate of ammonia (ammonium sulphate), 120 lbs. of coal tar and 1500 lbs. of coke.

The *coke*, which is obtained by so-called high temperature distillation (at about 1100°), has a calorific value of about 13,000 B.T.U. per lb. Although it may be used as a fuel in furnaces and closed stoves, it does not ignite or burn readily in an open fire-place. It is, therefore, not very suitable for ordinary domestic heating. If, however, the distillation is carried out at a temperature of 500°–600° C. (so-called low temperature carbonisation), a *semi-coke* is obtained which retains sufficient volatile matter to enable it to burn readily and without smoke in the ordinary grate. Considerable quantities of this low-temperature coke, having a calorific value of about 13,500 B.T.U. per lb., are now produced and sold under various names, *e.g.* coalite.

Not only does the nature of the coke vary according as it is produced by high-temperature or by low-temperature distillation, but marked differences are also found in the other products of the operation, the gas and the tar. These will be considered more fully presently.

**Solid Illuminants. Candles.**—The production of light depends in all cases, with the exception of electric light, on the process of combustion in air, and it is therefore only what one would expect, that man first made use of those naturally occurring substances and materials which can be burned without requiring previous special treatment. While the flame of burning wood was, perhaps, man's first illuminant, the vegetable oils, such as olive oil and rape-seed oil, furnished, from a very early period, the main light-giving material; and at a later date, the need of a vessel to contain the oil was done away with by using the solid animal fats, in the form of candles.

For the earliest candles, a solid animal fat was employed,

<sup>1</sup> Anthracite yields practically no volatile products on distillation.

such as ox-fat or tallow, and the candle was made by repeatedly dipping the wick into the melted tallow. At first, the wick was made from the dried pith of the rush (whence was derived the name *rushlight*), but later, wicks of cotton fibre were employed. From the manner in which they were made, these candles were called *dips*.

In the making of the modern candle, the fat or tallow is first "rendered," by boiling with acidified water in order to separate the fibrous matter from the fat, and the latter is then subjected to the action of superheated steam in presence of a little slaked lime or an acid. Thereby, as we shall learn more fully later, the fat is decomposed into glycerine and the acids with which it was combined—stearic, palmitic and oleic acids. After purification, the mixture of acids is distilled, and the solid acids separated from the liquid oleic acid by pressing. The solid thus obtained consists mainly of stearic acid or stearin, and forms, generally with the addition of a small quantity of paraffin wax, the material of the ordinary stearin candle of the present day. This candle has the advantage over the old tallow dip in being harder and cleaner to handle, in having a better appearance (white and opaque), in showing no tendency to bend or to gutter, and in burning with a bright and smokeless flame.

The paraffin wax, to which we have just referred, is itself also largely used for making candles. It is a white material which was, at first, chiefly obtained by heating in retorts, or distilling, the oil shale found in the Lothians, Scotland. Paraffin wax is now also produced in large quantities in Germany by distilling brown coal or lignite, and is likewise obtained from American, Galician, and especially from Burma or Rangoon petroleum. It consists of a mixture of compounds (*e.g.*  $C_{27}H_{56}$  and  $C_{30}H_{62}$ ) which contain only hydrogen and carbon, and are therefore called *hydrocarbons*; it thus belongs to an entirely different class of compounds from the fats or the fatty acids, all of which contain oxygen. Before being employed for the making of candles, the crude paraffin is subjected to a refining process for the purpose of obtaining a wax of higher melting-point and free from coloured impurities. The material so obtained is valued for its slightly translucent appearance, but it has the disadvantage, as compared with stearic acid or stearin, that when exposed to a warm atmosphere, it is liable to bend under its own weight.

The wax candles formerly so highly prized were made of bees-wax, a substance related in its composition to the fats and oils, and consisting mainly of a compound of palmitic acid with

an alcohol known as melissyl alcohol. Spermatet<sup>1</sup>, a similar compound obtained from the oil of the sperm whale (*physeter macrocephalus*), is another excellent but expensive material used in the manufacture of candles. Candles made of this material were long used as a standard measure of artificial light, on account of the large and regular flame with which they burn. The hard China wax, produced by a coccus, a small insect similar to the wood-louse, and various kinds of vegetable wax are also used for candle-making in China and Japan.

Although the materials of which candles are made are, of course, combustible, it should be remembered that they do not burn unless the temperature is raised to a point sufficiently high to cause them to pass into vapour; and it is the vapour which burns and so gives rise to the flame.

In the old tallow candles, the wick required to be snuffed from time to time; that is, the charred end of the wick had to be removed with a pair of special scissors. This was due to the fact that immediately surrounding the wick of the candle there is the unburnt vapour of the candle material, and this vapour cuts the wick off from contact with the atmospheric oxygen. Consequently, although the wick becomes charred by the heat of the flame, it is not consumed, because the oxygen of the air is not allowed access to it. The charred wick, therefore, continues to increase in length and there is conducted up into the flame more of the liquid fuel than can properly be consumed. The flame then burns dim and emits a large amount of smoke.

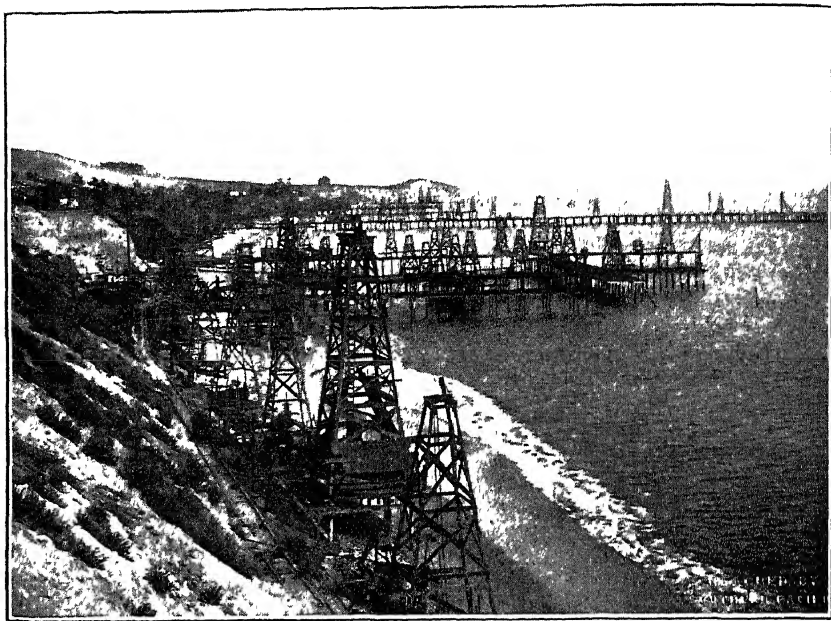
In 1825, it was shown by a Frenchman, CAMBACÈRES, that the necessity for snuffing could be obviated by the use of twisted or flat-plaited wicks. As the candle burns, the end of the wick, as every one may see by looking at a burning candle, curls or bends outwards to the edge of the flame, and coming, in this way, into contact with the oxygen of the air, it burns away, and so no snuffing is required.

**Liquid Fuels and Illuminants.**—Coal, it is recorded, was mined and used as a fuel in England as early as the thirteenth century, but it was not till the nineteenth century that the great natural deposits of the liquid fuel PETROLEUM,<sup>1</sup> occurring, more especially, in America and Russia, began to be exploited, for the production mainly of illuminants and lubricants; and the exploitation of these resources inaugurated a new era in the production and utilisation of energy.

The occurrence of a natural oil and of bitumen has been known from a very early period. The builders of the Tower

<sup>1</sup> From the Latin *petra* (rock) and *oleum* (oil).

of Babel, we are informed, used "slime" or bitumen (formed from petroleum by the loss of its more volatile constituents), as a mortar, and it is recorded in Genesis that the Vale of Siddim, where Lot pastured his flocks, was "full of slime pits." The conclusions of the commentators, therefore, appear not unreasonable when they attribute the destruction of Sodom and Gomorrah, which lay in this oil-bearing region, to a great conflagration of natural gas and oil, set free from a subterranean reservoir by some great earthquake. Classical writers, also,



*(Courtesy Southern Pacific Company)*

Oil wells near Summerland, California.

from Herodotus to Pliny, record the presence of oil in various regions, and describe its use both as an embrocation and, to some extent, also as an illuminant.

In America, the existence of small quantities of oil, seeping from the earth, had long been known in certain parts of the States of New York and Pennsylvania, and the oil had, by reason of its medicinal and curative properties, been used both internally and externally. It was not, however, till 1859 that Colonel E. L. Drake drilled the first oil-well at Titusville, Pennsylvania, for the purpose of winning the oil for use as an illuminant and

lubricant. Soon many other wells were sunk and the Pennsylvania oil-field became, for a time, the leading oil-field of the world. During the present century, other great oil-fields have been developed in America, more especially in Oklahoma, Texas, California and Wyoming, where the clusters of drilling and pumping derricks, rising from the desert or through the waters of the ocean, tell of the wealth concealed beneath the surface of the earth.

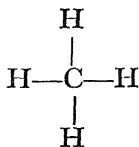
The increasing demand for oil, for use as an illuminant and lubricant, led also to the more active exploitation of the long-known oil resources of Baku, near the Caspian Sea, and of Galicia; and during the present century, more especially, the great and rapidly increasing demand for oil, for use as a fuel, linked up as it is with the phenomenal development of the automobile and aeroplane industry, with its deep and widespread effect on the social life of to-day, has stimulated an extraordinary activity in the search for and exploitation of new oil-fields in Mexico, Dutch East Indies, Burma, Persia and elsewhere.

Of the origin of petroleum, little can be asserted with confidence, but it is generally considered that the oil has been formed by the gradual decomposition, under the age-long action of heat and pressure, of deposits of marine animal and vegetable matter. On the other hand, the opinion has been expressed that it has been formed by the action of heat and pressure on certain types of coal. Whatever its origin may be, however—and it may have had various origins—petroleum occurs in pools between layers of impervious rock, and is associated with a gas, the pressure of which is, in some cases, sufficient to force the oil up through the bore-pipe so as to form a mighty fountain. In former days, before suitable means of control had been devised, much oil was thereby lost.

**Composition of Petroleum.**—Although the petroleum from different oil-fields may vary greatly in composition, it consists, essentially, in all cases, of a mixture of hydrocarbons, or compounds which contain carbon and hydrogen only. In the case of Eastern American petroleum, for example, the hydrocarbons belong, for the most part, to what is known as the methane series; but in the petroleum from other regions, hydrocarbons of a very different kind may occur.

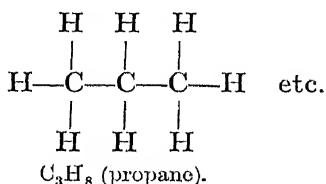
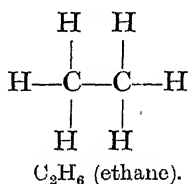
*Methane*, or marsh gas, is the lowest member of a long series of hydrocarbons, all of which have similar chemical properties and composition. The molecule of methane consists of one atom of carbon to which four atoms of hydrogen are united; and since an atom of carbon is never found to combine with

more than four atoms of hydrogen, the carbon is said to be saturated. Methane is spoken of, therefore, as a *saturated hydrocarbon*. Diagrammatically, we can represent the molecule of methane thus :



Methane is the inflammable gas which rises in bubbles when one stirs the mud of decaying vegetation at the bottom of a stagnant pool—hence the name *marsh gas*; and it is also the gas which, produced during the formation of coal, escapes from the coal-beds during mining and which, mixing with the air of the mine, constitutes the explosive mixture, *fire-damp*.<sup>1</sup> Methane, moreover, is the main constituent of the “natural gas” which escapes from the earth in various regions, as in Canada and America and in the region of Baku on the Caspian Sea, where the Holy Fire of the burning gas was for long a place of pilgrimage of the Persian Guebers or fire-worshippers. It is a gas which burns with only a slightly luminous flame; and it was to it that the pale flickering light known as *ignis fatuus* or “will-o’-the-wisp” was supposed to be due.

The compound methane, it has been stated, is the lowest member of a series of similar compounds, which arise owing to the fact that the element carbon is remarkable among all the elements in its property of combining with other atoms of carbon, and of thereby forming “chains” of carbon atoms. In this way, a series of compounds is obtained which may be represented by the diagrams :



A large number of such compounds are known, all of them saturated hydrocarbons, and it will be observed that the composition of each of them can be represented by the general formula  $\text{C}_n\text{H}_{2n+2}$ . The molecular composition of successive

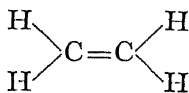
<sup>1</sup> That is, *fire gas* or *fire vapour*.

members, it will be seen, differs by one carbon and two hydrogen atoms.<sup>1</sup>

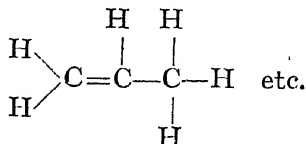
The first four members of the series, known as methane, ethane, propane and butane, are gases at the ordinary temperature. The succeeding members are liquids, which become less and less volatile, and boil, therefore, at higher and higher temperatures, as the molecular weight of the hydrocarbon increases. When the number of carbon atoms in the molecule is greater than sixteen, the compounds are solid at the ordinary temperature.

Owing to their chemical inertness, the hydrocarbons belonging to this series are spoken of as *paraffins*.<sup>2</sup>

It may be mentioned that other series of hydrocarbons are known which contain a lower proportion of hydrogen, and are therefore said to be *unsaturated*. Thus, if two hydrogen atoms are removed from each of the compounds of the methane series, hydrocarbons are obtained which can be represented by the formulæ :

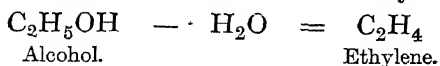


$\text{C}_2\text{H}_4$  (ethylene).



$\text{C}_3\text{H}_6$  (propylene)

These compounds belong to another homologous series of hydrocarbons, represented by the general formula  $\text{C}_n\text{H}_{2n}$ , and spoken of generally as the *olefines*. ETHYLENE occurs in the gas obtained by distilling coal, and some of the higher members of the series occur in certain types of petroleum. It is used as an anæsthetic and is best prepared by heating alcohol with phosphoric acid. The elements of water are thereby removed :



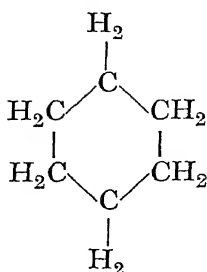
During the Great War, ethylene was largely used in the manufacture of what is known as *mustard gas*,  $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$ , a compound which is, however, not a gas but a liquid at the ordinary temperature.

Whereas Eastern American petroleum consists mainly of hydrocarbons belonging to the paraffin (methane) series, from  $\text{CH}_4$  up to  $\text{C}_{30}\text{H}_{62}$ , Californian and Russian petroleums contain

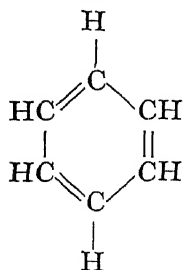
<sup>1</sup> A series of similar compounds in which the molecular composition of successive members differs by  $\text{CH}_2$  (one carbon atom and two hydrogen atoms), is known as an *homologous series*.

<sup>2</sup> From the Latin *parum* (little) and *affinitas* (affinity).

a large proportion of another series of hydrocarbons, represented by the formula  $C_nH_{2n}$ . These compounds, called *naphthenes*, contain less hydrogen than the hydrocarbons of the methane series; and although they are represented by the same general formula as the olefines, they differ from these in that the carbon atoms are not joined together in *open chains* but in *closed rings*, of five or six carbon atoms, as shown by the formula :



These hydrocarbons are akin to the substance benzene,  $C_6H_6$ , or



, but contain a higher proportion of hydrogen.

This compound, benzene, along with other similar hydrocarbons (*e.g.* toluene), is found in notable amounts in certain petroleum, such as those from Borneo, Persia and Burma.

*Crude petroleum* is generally a thick, yellow, brown or black liquid, which shows a green fluorescence. It contains, in solution, considerable quantities of natural gas, consisting chiefly of methane but containing also ethane, propane and butane. This gas is separated from the oil at the well-head and is distributed for domestic and industrial use as an illuminant and as a fuel.

**Fractional Distillation of Petroleum.**—After separation of the natural gas, the petroleum is pumped through pipe-lines from the oil-field to the refinery, where it is subjected to *fractional distillation*, in order to separate it into portions adapted for different purposes. When the crude petroleum is distilled, the lower and more volatile hydrocarbons pass over first; and by collecting the liquid which distils over at different temperatures,



a series of "fractions," as they are called, is obtained. Thus, the liquid which distils over up to a temperature of about  $70^{\circ}\text{C.}$ , is called petroleum ether and is largely used as a solvent and as a local anæsthetic owing to the cold produced by its evaporation. It consists mainly of pentane ( $\text{C}_5\text{H}_{12}$ ), but contains also a certain amount of hexane ( $\text{C}_6\text{H}_{14}$ ). The next fraction, distilling over between  $70^{\circ}$  and  $120^{\circ}\text{C.}$ , is called gasoline or petrol, and is used as a motor spirit and also for illuminating purposes (petrol-air gas). It is a mixture of hexane ( $\text{C}_6\text{H}_{14}$ ), heptane ( $\text{C}_7\text{H}_{16}$ ) and octane ( $\text{C}_8\text{H}_{18}$ ). At a higher temperature, from  $120^{\circ}$  to  $150^{\circ}\text{C.}$ , there distils over a fraction called petroleum benzine or benzoline,<sup>1</sup> which is used as a "dry cleaning" agent and as a solvent.

As the temperature of distillation rises, the hydrocarbons of higher boiling-point distil over. The fraction distilling between  $150^{\circ}$  and  $300^{\circ}\text{C.}$ , constitutes burning oil, kerosene or paraffin oil; that distilling between  $250^{\circ}$  and  $340^{\circ}\text{C.}$ , constitutes solar oil or gas oil, and is used for enriching coal gas and also in Diesel engines. Between  $340^{\circ}$  and  $500^{\circ}\text{C.}$ , oils of various grades distil over and are used as lubricating oils and for burning under boilers. From the highest fractions of all one obtains vaseline, and in some cases, solid paraffin, which is used for making candles, waterproofing paper, and other purposes. On heating the residue to a high temperature, a pure form of coke is obtained.

As a result of the distillation process, Mid-continent American petroleum, for example, yields about 4 per cent. of gas, 25 per cent. of naphthas (gasoline and benzoline), 15 per cent. of kerosene, 40 per cent. of gas oil, 12 per cent. of solid paraffin and lubricating oils and 4 per cent. of coke. The relative amounts of the different fractions, however, vary with the type of petroleum. Thus Borneo and Sumatra petroleum may yield as much as 40 per cent. of the volatile naphthas.

**Kerosene as an Illuminant.**—Since paraffin oil, or kerosene, contains a relatively large amount of carbon,<sup>2</sup> it burns with a smoky flame, owing to incomplete combustion, unless there is a liberal supply of air. When this oil is used as an illuminant, therefore, the flame is surrounded by a chimney whereby a draught of air is created, and oxygen is thus brought in larger amount to the flame; and in the case of lamps with a circular wick, a tube must also be provided through which air can pass to the *inner* surface of the flame.

<sup>1</sup> Not to be confused with the compound benzene,  $\text{C}_6\text{H}_6$ .

<sup>2</sup> The hydrocarbon  $\text{C}_{13}\text{H}_{28}$ , for example, which boils at  $216^{\circ}\text{C.}$ , contains 84.7 per cent. of carbon.

In the early days after the introduction of mineral oil as an illuminant, explosions and fires were not infrequent, and these led to the introduction of special legislation to regulate the use of such oil. The accidents which occurred were due mainly to the insufficient removal of the more volatile constituents of the petroleum, and these, mixing with the air in the oil reservoir of the lamp, formed an explosive mixture which became ignited by the flame. To obviate such risks, it has been enacted that only such oil shall be used as does not give off an inflammable vapour below a certain temperature. This is tested by heating the oil in a special apparatus under specified conditions, and determining the temperature at which, on passing a light over the mouth of the vessel containing the oil, a flash of flame is seen. This is known as the flash-point of the oil, and in Great Britain it has been enacted that the flash-point of burning oil must not be below 73° F., when determined by what is known as the "closed" test.

**Oil Fuel.**—Until well into the twentieth century, petroleum was of importance chiefly as furnishing illuminants and lubricants. During recent years, however, owing more especially to the rapid increase in the number of motor cars, the chief value of petroleum depends on its being a source of fuel supply. Not only does gasoline or petrol constitute a fuel for which the demand threatens to exceed the supply, but the higher boiling portions of petroleum, which distil over after the kerosene, form a fuel which can be burned under boilers and used for raising steam. Since 1 lb. of fuel oil has a calorific value of about 19,500 B.T.U.—about one and a quarter times greater than that of anthracite—and since oil possesses many advantages over coal in the matter of cleanliness, control of consumption, stowage room, etc., its use as a fuel, especially for ocean steamers, has greatly increased.

**Gasoline as a Fuel.**—It is, however, in the use of gasoline or petrol as a fuel for the internal combustion, motor car and aeroplane engine that the greatest developments have taken place. As a result of this development, the 25 per cent. or so of naphtha yielded by the fractional distillation of crude petroleum was quite insufficient to meet the demand. Some means of increasing the supply, therefore, became necessary, and, in recent years, this supply has been greatly increased by the process of "cracking"<sup>1</sup> the relatively unimportant gas oil which forms in some cases a large proportion of the distillation

<sup>1</sup> The term "cracking" was suggested by the noise which is made by oil which has inadvertently been allowed to remain in an overheated still.

product of crude petroleum. When this oil is heated under pressure to a sufficiently high temperature ( $380^{\circ}$  C. or more), the relatively large molecules, say,  $C_{20}H_{42}$ , are broken down into the simpler molecules of the hydrocarbons which constitute gasoline. Considerable quantities even of kerosene, for which, owing to the increasing use of gas and electric lighting, the demand has diminished, are similarly "cracked," in order to meet the ever-increasing demand for motor fuel. In the motor fuel obtained by "cracking" there are present, not only olefines but also a certain amount of the so-called aromatic hydrocarbons (benzene, toluene, etc.), and these are of value because they help to prevent the unpleasant phenomenon of "knocking."

When petrol or gasoline is used for the production of power in an internal combustion engine, it is the potential energy of the mixture of petrol vapour and air that is converted into the energy of motion. When the combustible mixture is compressed by the piston, at the expense of the energy stored in the fly-wheel, a spark, produced at the sparking-plug, ignites the mixture, which then burns rapidly, but not explosively. Not only do the products of combustion occupy a greater volume than the combustible vapour and air, but the higher temperature produced by the combustion causes a still greater expansion of volume. A high pressure is thereby exerted on the piston, the pressure on the piston having the character of a continuous push and not that of a blow. The mechanical energy which is thereby produced will of course depend on the temperature, and this, in turn, depends on the heat of combustion of the petrol. Since this is very high—about 18,700 B.T.U. per lb. or about 135,000 B.T.U. per Imperial gallon—petrol or gasoline is a valuable fuel.

The efficiency with which the heat energy of combustion is converted into mechanical work, increases with the degree to which the combustible gases are compressed. For a particular fuel, however, there is a degree of compression which cannot be exceeded without the unpleasant and harmful "pinking" or "knocking" taking place. This knocking is due to the fact that the wave of combustion passes after a certain time into a much more rapid wave of explosion, and the continuous push of the expanding gases on the piston passes into a sudden blow, which produces great stresses on the moving parts. In the case of the saturated hydrocarbons, belonging to the methane series, detonation takes place with comparatively low compression, but the addition of naphthenes, and still more of benzene, permits a higher compression to be used without knocking.

The increase of efficiency of an internal combustion engine

with compression is so great that it may compensate for a considerable diminution of the calorific value of the fuel. Alcohol (spirits of wine), which has the formula  $C_2H_5OH$ , has a calorific value of only 10,350 B.T.U. per lb. or 84,900 B.T.U. per gallon, but it will stand a much higher compression than petrol. One can, therefore, obtain with alcohol a thermal efficiency of 30 per cent., whereas with petrol a thermal efficiency of only 15–20 per cent. is obtained.

**Production of Liquid Fuel from Shale and Coal.**—The natural reserves of oil are not inexhaustible, and it has even been predicted by experts that the petroleum reserves of America—the country of greatest oil production—will be exhausted by 1935. Even though this forecast should prove too pessimistic, the world must face the ultimate and perhaps not very distant exhaustion of the natural deposits of oil, and the question, therefore, presents itself whether any substitute can be obtained. Fortunately, rays of hope issue from various quarters.

In Scotland, ever since 1860 or thereby, mineral oil has been obtained by heating a carbonaceous shale, called *oil shale*. Although containing no oil as such, a ton of this shale may yield, when distilled, about 30 gallons of oil, from which, by fractionation, motor spirit, burning oil, fuel oil, lubricating oil and solid paraffin can be obtained. Since deposits of oil shale, sometimes enormous in extent,<sup>1</sup> occur in many different countries, it will be possible to obtain abundant supplies of oil fuel—at a greater cost, it may be, than at present—when the oil wells shall have ceased to flow.

From coal, also, fuel oil may be obtained, and is, in fact, being obtained by various processes. By the low temperature carbonisation of bituminous coal (p. 197), a tar is produced from which one can obtain, by fractional distillation, motor spirit, fuel and lubricating oils, similar to those obtained from petroleum; whereas, by high temperature carbonisation of coal, a tar is produced from which benzene, and a number of other substances of value in chemical industry, are obtained. Although not used as motor spirit by itself, benzene is used for mixing with petrol.

An oil, somewhat like natural petroleum, can, as the German chemist F. BERGIUS, and others, have shown, be obtained by suitably heating coal with hydrogen gas under pressure. Large quantities of oil are, in fact, being produced in Germany at the present day by this process of *berginisation*.

<sup>1</sup> Such deposits, amounting to untold millions of tons, are known, for example, in the States of Indiana, Colorado and Utah in America.

By these and other methods, chemists are preparing to meet the change in conditions which will arise when the natural deposits of petroleum are exhausted.

**Gaseous Fuels and Illuminants.**—Petroleum, as we have seen, is always associated with a “natural gas,” consisting mainly of the hydrocarbon, methane, although other gaseous hydrocarbons are also present in varying amount. In various regions, especially in the United States and Canada,<sup>1</sup> great reservoirs of natural gas<sup>2</sup> are sometimes found, unassociated with oil, and this gas has been used for many years, at Pittsburgh, for example, not only for illuminating purposes but also, and mainly, as an industrial fuel in iron and steel manufacture, for the melting of glass and in other industrial operations. As a fuel, natural gas, which, it is stated, was used even in ancient times by the Chinese, is of great importance on account of its high calorific value. This amounts to over 1000 B.T.U. per cubic foot, or twice as much as that of the gas obtained by the high temperature distillation of coal.

Sometimes the pressure under which the natural gas occurs is very high, even reaching a value of more than 30 atmospheres; and the amount contained in the subterranean gas-holders is inconceivably large. In the case of one gas well in Kansas where the gas was ignited by lightning, the pressure of the gas was such that a great torch of flame 225 feet in height was produced, the heat of which was so great that even in the February climate of Kansas, it is stated, the neighbouring trees began to break into leaf. Although the fire continued for thirty-five days, consuming, it was estimated, over two million million cubic feet of gas, the pressure of the gas in the field was not reduced.

By far the most important gases, however, used at the present day for the production of heat and light, are those which are obtained, by one process or another, from coal, and more especially the gas which is obtained by heating coal in closed vessels or “retorts,” out of contact with the air.

Although coal had been used as a fuel as early as the beginning of the fourteenth century, it was not till 1680 that the distillation of coal in closed vessels was carried out by the alchemist, Johann Joachim Becher, whose views concerning the presence of a *terra pinguis* in combustible bodies led Stahl to the formulation of the Phlogiston theory. Becher's purpose in carrying

<sup>1</sup> One notable gas well was also found at Roma, Queensland, Australia, which yielded gas at the rate of a million cubic feet a day.

<sup>2</sup> This natural gas sometimes contains as much as 3–4 per cent. of helium. In Colorado, a content of 7 per cent. has been found.

out the distillation of coal was the production of pitch and tar for the treatment of wood and of rope, and the production of coke for domestic heating and the smelting of metals.

A few years later, about 1688, the Rev. JOHN CLAYTON, D.D., a Yorkshire clergyman who later became Dean of Kildare, after investigating the escape of an inflammable gas from a coal-seam, made the following communication to the Hon. Robert Boyle :<sup>1</sup> "I then got some Coal from one of the Pits nearest thereunto, which I distilled in a Retort in an open Fire. At first there came over only *Phlegm*, afterwards a black *Oil*, and then likewise a *Spirit*, which I could nowadays condense, but it forced my Lute, or broke my Glasses. Once, when it had forced the Lute, coming close thereto, in order to try to repair it, I observed that the Spirit which issued out caught Fire at the Flame of the Candle, and continued burning with Violence as it issued out. . . . I then filled a good many Bladders therewith. . . . And when I had a Mind to divert Strangers or Friends, I have frequently taken one of these Bladders, and pricking a Hole therein with a Pin, and compressing gently the Bladder near the Flame of a Candle till it once took Fire, it would then continue flaming till all the Spirit was compressed out of the Bladder ; which was the more surprising, because no one could discern any Difference in the Appearance between these Bladders and those which are filled with common Air."

Although the formation of a combustible gas by the distillation of coal was thus known before the end of the seventeenth century, it was not till a hundred years later that the process was developed for the production of an illuminating gas for general use. The credit for this development belongs to WILLIAM MURDOCH (1754-1839), who was born at Lugar in Ayrshire, and became associated with the engineering firm of Messrs Boulton and Watt, Birmingham. In 1792, he lighted his house at Redruth, in Cornwall, with coal gas ; and it was at the works of Boulton and Watt at Soho, Birmingham, that coal gas was first used (in 1798) on a large scale as an illuminant. It was, however, only after the lapse of ten to fifteen years that the gas began to be publicly and generally used. In 1810, a German, Winzer, who on his arrival in England changed his name to Winsor, founded the Gas, Light and Coke Company ; in 1813, Westminster Bridge, and, in 1816, the greater part of London, were lighted by gas. The introduction of gas lighting met with much opposition, as one can understand, on the part of the tallow

<sup>1</sup> *Phil. Trans. Roy. Soc.*, 1739, 41, 59.

chandlers and sellers of whale oil—at that time used as an illuminant; but after a time the new method of lighting was welcomed. The great change which was thereby effected in the appearance of the towns and in the comfort of the people, is described by a writer in the early nineteenth century: "We all remember the dismal appearance of our most public streets previous to the year 1810; before that time, the light afforded by the street lamps hardly enabled the passenger to distinguish



Introduction of GAS!! or Throwing a NEW LIGHT on the Subject.  
(After a Print by G. Cruikshank, 1815.)

"A street scene with the road broken up to lay down gas pipes. On a barrow belonging to the Gas Company, its projecter Winzer is standing and holding forth on the merits of gas and its capabilities to a party of bystanders who deride him. The shops are closed through the impassable state of the thoroughfare."—*British Museum Catalogue*.

a watchman from a thief, or the pavement from the gutter. The case is now different, for the gas-lamps afford a light little inferior to daylight and the streets are consequently divested of many terrors and disagreeables, formerly borne with because they were inevitable."

In the manufacture of illuminating gas, the coal is heated in large fire-clay retorts at a temperature of  $1000^{\circ}$ – $1100^{\circ}$  C., and the products of decomposition are led away by a pipe the mouth of which dips under the surface of water contained in what is





The ammonia present in the gas dissolves for the most part in the water produced, and the remainder is removed by passing the gas through "scrubbers." The gas still contains a number of substances the presence of which would be deleterious, the most important of these being sulphuretted hydrogen,  $\text{H}_2\text{S}$ , and carbon dioxide. The sulphuretted hydrogen is harmful because it gives rise, in the burning gas, to sulphur dioxide<sup>1</sup> (the pungent gas formed when sulphur burns in air), which exercises a destructive action on plants, furniture, etc.; and the presence of carbon dioxide is objectionable because it lowers the heating and illuminating power of the gas. To free the gas from these impurities, therefore, it is passed, first of all, through a series of boxes containing trays covered with slaked lime which combines with and so removes the carbon dioxide; and then through another series of boxes containing oxide of iron,  $\text{Fe}_2\text{O}_3$ , which removes the sulphuretted hydrogen, by forming with it the compound, sulphide of iron,  $\text{Fe}_2\text{S}_3$ . When conversion of the oxide into sulphide is complete, the material is incapable of removing any more sulphuretted hydrogen, but it can be revived by exposure to the air. Through this exposure, the oxygen of the air reconverts the sulphide of iron into oxide of iron, and the sulphur is set free. In this way the oxide of iron may be used repeatedly, until at length the accumulation of sulphur renders it inefficient. The material, however, still has its uses, for it is sold to the manufacturer of sulphuric acid, who utilises it in a manner which we shall learn later.

After undergoing the various processes of purification, the gas passes to the gas-holder, and is then ready for distribution to the consumers. Although the composition of the gas supplied by different works is by no means the same nor invariable even in the case of the same works, the following numbers may be taken as representing an average composition of coal gas:

## COMPOSITION OF COAL GAS.

		49 per cent. by volume.
Hydrogen . . . . .		35
Methane . . . . .		4
Unsaturated hydrocarbons (ethylene, etc.). . . . .		5
Carbon monoxide . . . . .		0.5
Carbon dioxide . . . . .		6
Nitrogen . . . . .		0.5
Oxygen . . . . .		

Coal gas, then, it will be seen, is a mixture of a number of gases, and of these carbon dioxide, nitrogen, and oxygen represent what we may call impurities; they act merely as diluents and lower the illuminating power of the gas.

<sup>1</sup> As shown by the equation:  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2$ .

Of the combustible gases present in coal gas, hydrogen burns with a non-luminous, scarcely visible flame; carbon monoxide, with a non-luminous flame of a bright blue colour; and methane, with a flame which has only a slight illuminating power. Ethylene, however, burns with a strongly luminous flame, and it is to this gas, and to the other unsaturated hydrocarbons present in small amounts, that the luminosity of a coal-gas flame is mainly due. Among the unsaturated hydrocarbons present, there may be mentioned acetylene (p. 218) and benzene (or benzole, to give it the name by which it is known in commerce), the vapour of which burns with a luminous flame and with the production of a large amount of soot.

What, then, is the explanation of the luminosity of the flame of burning coal gas, or of a candle, or of petroleum? The answer is that which was given long ago by Sir Humphry Davy: The luminosity depends on the decomposition of the hydrocarbons with liberation of particles of carbon which are then raised to incandescence by the heat of the burning gases. The presence of this finely divided carbon can, indeed, be readily shown by bringing a cold object into the luminous part of the flame; it becomes coated with soot. These carbon particles, however, do not escape into the air, but on reaching the edge of the flame where they come into contact with the oxygen of the air, they are completely burned to the invisible gas carbon dioxide. And so, on examination, one sees in these flames three zones: an inner non-luminous zone of unburnt gas or vapour; a luminous zone in which the carbon particles are raised to incandescence; and a very faint outer zone surrounding the flame, in which complete combustion of the carbon particles takes place.

From the explanation which has just been given, it will readily be understood that the luminosity of a flame will be increased by increasing the proportion of carbon-yielding substances in the burning gas; and hydrocarbons, and more especially unsaturated hydrocarbons, which contain a relatively large proportion of carbon, will be the most effective substances to use. By such additions it is possible to "enrich" a poorly luminous gas, a fact which is made use of at the present day in many of the larger gas-works.

Not only can a combustible gas be manufactured by the distillation of coal, but when steam is passed over red-hot coke, a gas is obtained which is a mixture of hydrogen and carbon monoxide:



Although this gas mixture, known as *water gas*, has no illuminating power, it can be manufactured at a small cost, and after being enriched by the addition of gas oil (p. 205), or of unsaturated hydrocarbons, obtained by the decomposition or "cracking" of oil at a high temperature, it is added (as *carburetted water gas*) to the gas obtained by the distillation of coal.<sup>1</sup>

Formerly, when coal gas was used almost entirely as an illuminant, gas-producing companies had to supply gas of a certain minimum illuminating power; but at the present time coal gas is mainly employed as a domestic and industrial fuel for the production of heat. The illuminating power standard has therefore been abandoned in Great Britain, and gas-producing companies may supply gas of varying quality, but the charge to the consumer may be made only on the basis of the heat value of the gas. Greater freedom is in this way given to the producer, and the consumer pays for the amount of heat energy or the number of *therms* he receives, 1 therm being equal to 100,000 B.T.U.

Coal gas, produced by high temperature carbonisation, has a calorific value of about 480–520 B.T.U. per cubic foot; while that produced by low-temperature carbonisation has a value of 800–1000 B.T.U. per cubic foot. The calorific value of water gas which is largely used as an industrial fuel, is about 280 B.T.U. per cubic foot.

When coal gas is used as a fuel for heating purposes, it is important that combustion take place rapidly and completely without the separation of carbon particles, and this result is secured if the gas, before being burned, is mixed with a suitable amount of air. The molecules of the combustible gas then find oxygen with which they can combine, ready at hand, so to say. In such a case the flame is non-luminous and smaller, but much hotter, than the ordinary luminous flame. This principle was made use of by the German chemist BUNSEN in the burner which goes by his name, and is applied in gas fires, gas cookers, etc. (Figs. 44 and 45). In the Bunsen burner, the gas issues from a jet which is surrounded by a wider tube, near the foot of which holes are pierced; and through these air is drawn into the burner by the uprush of gas. The gas thereby becomes mixed with air, the amount of which necessary to ensure complete combustion can be regulated by enlarging or diminishing the

<sup>1</sup> Owing to the large amount of the very poisonous carbon monoxide present in water gas, great precautions against leakage should be taken when this gas is used for domestic purposes.

size of the air openings. If too much air is admitted to the gas, the mixture becomes explosive, and the flame strikes back to the jet where the gas enters the burner. If this occurs, the gas must be at once turned out, as incomplete combustion takes place and products of a very poisonous character are formed. These, fortunately, betray their presence by a powerful and unpleasant odour.

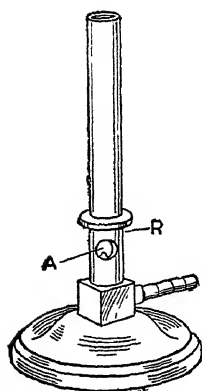


FIG. 44.—Bunsen burner.

A, air-hole by which air can pass into the tube and mix with the gas which enters at the small jet seen through the opening. The supply of air can be regulated by means of the movable ring, R.

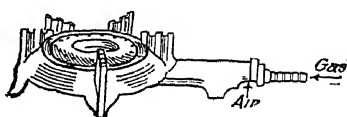


FIG. 45.—Gas cooker, constructed on the principle of the Bunsen burner.

as a diluent and so cools down the flame. One cannot, however, in this case make use of the ordinary burner, for the mixture of oxygen and coal gas would be explosive, and the flame would at once “strike back.” A burner of special construction is therefore employed which allows of a jet of oxygen being blown into the gas as it burns at the mouth of the burner.

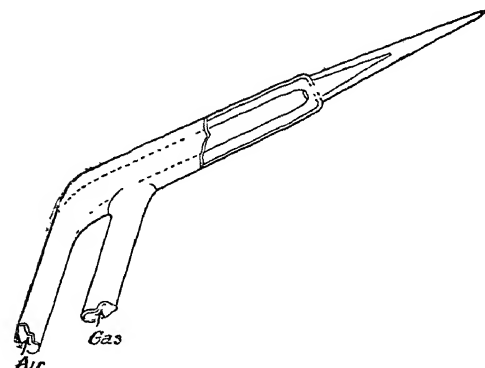


FIG. 46.—Blowpipe.

When the gas is burning at the mouth of the wider tube, air or oxygen is blown into the flame through the inner tube.

There is thus obtained what is known as the oxy-coal-gas blowpipe flame (Fig. 46). If this flame is allowed to impinge on a highly refractory material like quicklime, the latter is raised to a brilliant incandescence, producing the well-known lime-light. (Nowadays, the oxide of the rare metal zirconium is largely used in place of lime.)

For a number of years the position of coal gas as an illuminant has been persistently assailed by electricity; and it is certain that it could not have maintained itself, even as it has, but for the invention of the familiar incandescent mantle. This invention, it is important to bear in mind, we owe to a purely scientific investigation of the oxides of the rare metals, which was carried out by AUER VON WELSBACH in the laboratory of Bunsen in the University of Heidelberg in 1884.

In the course of his investigations, von Welsbach was struck by the fact that some of the oxides of the rare metals emitted an exceptionally brilliant light when incandescent; and at once his mind grasped the potentialities of the fact. A scientific discovery, however, is one thing; to make that discovery of practical utility is quite another; and in the present case, as in all cases, a large amount of patient and careful investigation had to be carried out before the incandescent mantle could be made a commercial success and be brought to its present state of perfection.

To make the discovery of practical utility, "mantles" or "stockings" of woven cotton, artificial silk, or ramie fibre (fibre produced from a plant of the nettle class), are soaked in a solution containing the nitrates of thorium and cerium<sup>1</sup> in the proper proportions. These mantles are then dried and incinerated, whereby the fibre is burned away and the nitrates are converted into a mixture of the oxides of the metals, which form a skeleton work preserving the shape of the mantle. On suspending this in the hot, non-luminous flame of a special burner constructed on the principle of the Bunsen burner, the mantle is raised to incandescence and emits a brilliant white light, many times greater than that given by the old flat flame consuming the same amount of gas. From a careful investigation it was found that the best results are obtained when the oxides are present in the proportion of 99 per cent. of thoria (thorium oxide) to 1 per cent. of ceria (cerium oxide). Neither thoria itself nor ceria itself has much light-giving power; and any variation in the proportions of the two oxides from those given, is accompanied by a diminution in the light-giving power of the mantle.

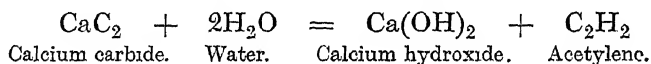
The most plausible explanation which has so far been advanced of the effect produced by the ceria, is that the particles of ceria are embedded in a badly conducting mass of thoria, which

<sup>1</sup> The chief source of these elements is a mineral known as monazite, which is found in various parts of the world, but more especially in Brazil and at Travancore, India.

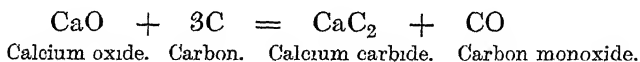
allows of the ceria being heated up to a point of brilliant incandescence; and further, the ceria possesses the property of accelerating the combustion of the gas, so that the combustion is concentrated or focussed on the small particles of ceria. As a consequence, the temperature of these particles rises above the average temperature of the mantle, and the brightness of the incandescence is thereby increased. This action of the ceria is spoken of as a *catalytic* action, about which we shall have more to say later. Ceria, however, is a substance which radiates heat rapidly, and if present in the mantle in larger amounts, the loss of heat by radiation is so great that the catalytic action is more than counterbalanced, and the illuminating power of the mantle is diminished.

Incandescent mantles are employed not only with coal gas but also with a combustible mixture of petrol and air; and petrol-air gas is now largely installed in houses in country districts remote from centres of coal-gas manufacture.

One other illuminant, the use of which depends on the process of combustion in air, must be mentioned, namely, **acetylene**, a gas which is readily obtained by the action of water on a compound of calcium and carbon, known as calcium carbide:



Calcium carbide is obtained by heating to a high temperature a mixture of quicklime (calcium oxide) and carbon in the form of anthracite coal or coke, and is formed in accordance with the equation:



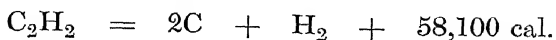
The preparation is carried out in a special type of furnace in which the high temperature necessary is obtained by means of the electric arc,<sup>1</sup> and owing to its use for the production of acetylene and for other purposes, carbide is now manufactured in large quantities in most civilised countries.

Acetylene is an unsaturated hydrocarbon, having a relatively large proportion (over 92 per cent.) of carbon, as is shown by its formula  $\text{C}_2\text{H}_2$  or  $\text{CH}\equiv\text{CH}$ . Under ordinary conditions the gas burns with a luminous and very smoky flame, but by using a special burner which ensures the admixture with the gas of a small amount of air, a white intensely luminous flame is obtained.

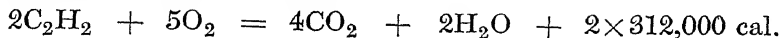
Acetylene is an endothermic compound, that is, it is formed

<sup>1</sup> A temperature estimated at about 3000° C. can in this way be obtained.

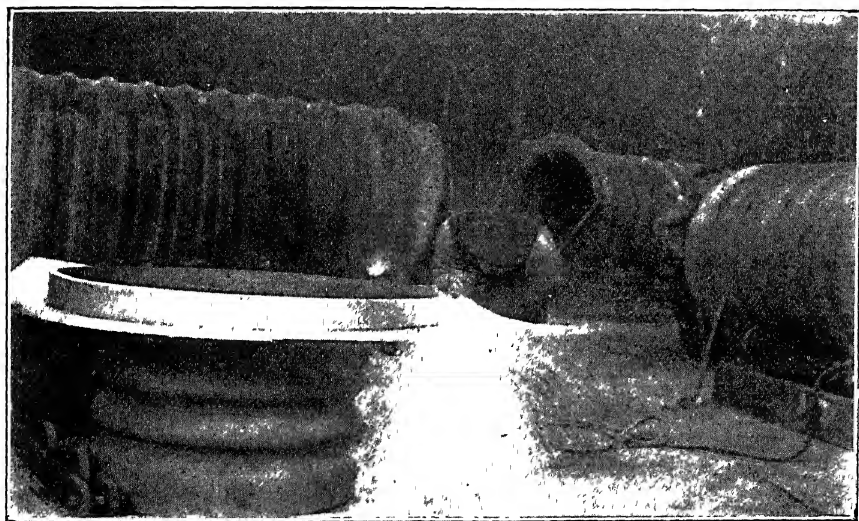
- from its elements with absorption of heat. When acetylene decomposes, therefore, heat is liberated :



Consequently, when acetylene burns in air or in oxygen, the heat of decomposition is added to the heat of combustion of the carbon and hydrogen present, and a very large amount of heat is therefore evolved. Thus :



By injecting oxygen into a flame of acetylene, therefore, a very high temperature, about  $3480^\circ \text{C.}$ , can be obtained. and this



(Courtesy British Oxygen Co., Ltd.)

Cutting steel by oxy-acetylene flame.

fact has received important applications. If, for example, the oxy-acetylene flame is allowed to impinge on a piece of iron, the metal is heated locally to bright redness, and if a fine jet of oxygen is then directed against the red-hot metal, the iron is oxidised to oxide of iron which melts in the intensely hot blow-pipe flame, and flows away like water. By this means one can even cut through large steel rods, shafts, plates or girders as easily as a knife will cut through cheese, and with a cut almost as fine.

## CHAPTER XIV

### HYDROGEN, WATER AND HYDROGEN PEROXIDE

#### HYDROGEN

HYDROGEN, so far as is known, was first prepared in the sixteenth century by Paracelsus, who noticed that when sulphuric acid was poured on iron, bubbles of a gas arose "which burst forth like the wind." At that time, the only gas recognised was atmospheric air, and Paracelsus assumed that the gas given off in his experiment was air. Towards the end of the seventeenth century, Boyle collected a quantity of the gas in a bottle and showed that it differed from ordinary air in being inflammable. It is, however, to the great scientific recluse, Cavendish, that we owe the first systematic investigation (in 1766) of "inflammable air," as he called it, and the discovery, in 1781, of the fact that when this gas burns in air or in oxygen, *water* is produced. This fact showed that, according to the explanation of combustion given by Lavoisier, water is a compound of "inflammable air" and oxygen; and it led Lavoisier to give to the "inflammable air" its present name of *hydrogen*.<sup>1</sup>

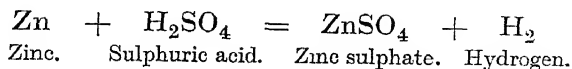
Although it is present in the flaming gases of the sun's chromosphere and in the gases emitted by volcanoes, and is produced also by the putrefactive decomposition of animal and vegetable matter, hydrogen is too light a gas to be retained in the atmosphere of the earth. It occurs, therefore, on the earth, almost entirely in a state of combination. Of the compounds of hydrogen, water is, of course, the most important, and the most abundant.

**Preparation of Hydrogen.**—On a small scale, this gaseous element may be prepared by the method used by Boyle and by Cavendish, that is, by the action of zinc or of iron on dilute sulphuric acid or dilute hydrochloric acid, the preparation being conveniently carried out in what is known as Kipp's apparatus (Fig. 47). As the gas is only slightly soluble, it may be collected in the pneumatic trough over water. When zinc

<sup>1</sup> From the Greek ὑδωρ (hydōr), water; and γεννάω (gennaō), I produce.



and sulphuric acid are used the reaction is represented by the equation :



For the large-scale production of hydrogen, of which enormous quantities are now consumed in various industries, this process is far too costly, and the gas is therefore obtained, by one means or another, from water. Various metals, such as sodium, potassium and calcium, decompose water vigorously even at the ordinary temperature;<sup>1</sup> but they also are too costly to be used industrially. It has, however, long been known that, at a red heat, iron decomposes steam with production of hydrogen;<sup>2</sup> and this process is one which is sometimes made use of for the industrial production of hydrogen. Similarly, carbon (coke) at a high temperature, as we have already seen (p. 214), decomposes water vapour, but as the oxide of carbon is gaseous, a mixture of carbon monoxide and hydrogen (water gas) is obtained. If this mixture is compressed and cooled by means of liquid air, the carbon monoxide and the other gases (air, etc.) which may be present as impurities, are liquefied, whereas the hydrogen, which is much less readily condensable, remains as a gas. Since by another process, also, to which reference will be made later (Chap. XX), hydrogen can be obtained in a pure state from water gas, this mixture is, on account of its comparative cheapness, most extensively employed as a source of hydrogen in industry.

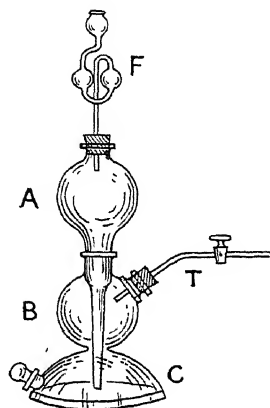
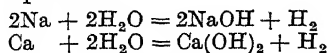


FIG. 47.—Kipp's apparatus.

Zinc plates are placed in the compartment, B, and dilute sulphuric acid is poured in through the funnel, F. The acid fills C and rises into B, where it comes into contact with the zinc. The hydrogen which is evolved passes out through the tube, T. On closing the tap on the tube, T, the acid is forced out of B by the pressure of the hydrogen, and the evolution of gas ceases.

<sup>1</sup> According to the equations :



The alloy of lead and sodium known as *hydrona*, is more convenient to handle than sodium itself, and may be used in place of this metal.

<sup>2</sup> According to the equation:  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ . The oxide of iron which is formed in this process is the so-called magnetic oxide and is different from rust, which is an oxide of the composition  $\text{Fe}_2\text{O}_3$ .

In places where electric power can be obtained sufficiently cheaply, the simplest process for the production of hydrogen is by the *electrolysis* of water. Although this process will be discussed more fully at a later point (Chap. XVII), it may here be said that when an electric current is passed through water, to which, say, sulphuric acid or caustic soda has been added, decomposition of the water takes place, and hydrogen is evolved at one of the metallic wires or plates (*electrodes*) which lead the current into the water. At the other electrode, oxygen is

evolved. The process can be demonstrated, on a small scale, by means of the apparatus shown in Fig. 48. The volume of hydrogen, it is found, is twice the volume of oxygen.

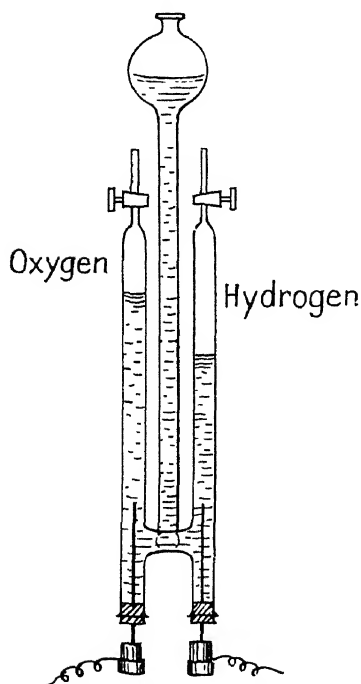


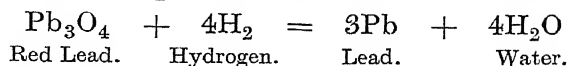
FIG. 48.—Electrolytic decomposition of water.

**Properties of Hydrogen.**—Although hydrogen is a colourless and odourless gas, and is, therefore, indistinguishable from the air, so far as our senses are concerned, it differs markedly from the air in being a combustible gas. When a light is applied to a jar of hydrogen or to a jet of the gas, the hydrogen burns with a non-luminous flame; and if a cold object, such as a beaker of water, is held above the flame, water condenses on the cold surface. When hydrogen and oxygen are mixed together and a light is applied to the mixture, combination takes place with explosive violence, and for this reason great care has to be exercised when one is handling this gas. This explosive combination of hydrogen

and oxygen can be demonstrated without danger by passing a mixture of the two gases through a tube into a quantity of soap solution contained in a mortar. A mass of bubbles is thereby formed, and on touching these with a lighted taper, combination of the gases takes place with a loud noise.

Hydrogen can combine not only with elementary oxygen but also with the oxygen present in compounds. Thus, when it is passed over a metallic oxide heated to a moderately high temperature, it combines with the oxygen and the oxide is con-

verted to metal. When red lead,  $\text{Pb}_3\text{O}_4$ , for example, is heated in a current of hydrogen, lead and water are formed, thus :



Hydrogen, therefore, removes the oxygen from the oxide of lead, and this process, which is clearly the reverse of the process of oxidation, is called *reduction*. Hydrogen is said to be a *reducing agent*; and since the reducing agent is itself oxidised in the process, it is clear that the processes of oxidation and reduction are complementary. It is of historical interest to note that phlogistonists identified hydrogen with phlogiston. Thus, Priestley, who in 1783 first observed the reduction of red lead by hydrogen, drew the conclusion that since the hydrogen converted the calx (oxide) into a metal, "it could be no other than that to which chemists had unanimously given the name phlogiston. Consequently, phlogiston is the same thing as inflammable air."

Hydrogen is a very light gas—it is 14.4 times lighter than an equal volume of air—and is therefore widely employed for the purpose of filling balloons and dirigible air-ships. A rough calculation will give an idea of the lifting power of hydrogen. Since one million cubic feet of hydrogen (at N.T.P.) weigh nearly 2.5 tons, the weight of an equal volume of air will be about 36 tons. A million cubic feet of hydrogen, therefore, will have a lifting power of about  $36 - 2.5 = 33.5$  tons.

Hydrogen has the property of dissolving in or of being *occluded* by certain metals, more especially by the metal palladium, which, even at the ordinary temperature, can occlude 600 times its volume of the gas. The hydrogen is expelled on heating the metal to redness.

It has already been pointed out (p. 182) that when hydrogen burns in air or oxygen, a large amount of heat is evolved. The oxy-hydrogen blowpipe flame (see Fig. 46, p. 216) is, therefore, like the oxy-acetylene flame, made use of for the purpose of producing a high temperature—a temperature reaching, under suitable conditions,  $2500^\circ \text{C.}$ —and finds application for the melting of platinum and other refractory metals and for the production of the so-called "lime-light" (p. 216).

## WATER

Water, one of the most abundant and widely distributed substances in nature, is, of course, familiar to all. Not only does it form the great oceans and lakes and rivers, and the

enormous ice masses of the Polar areas, but, in the form of vapour, it is everywhere around us in the air. Moisture permeates even the solid mass of the earth, and the Greek philosopher, Thales, as we may remember, impressed by the all-pervasiveness of water, regarded it as the universal principle underlying all forms of matter.

In water we have a liquid unique in its properties and indispensable to animal and vegetable life. In this liquid all living tissues are bathed, and it is in an aqueous *milieu* that all life processes occur. The high specific heat and latent heat of vaporisation of water form powerful safeguards against a too rapid or too excessive change in body temperature, and so secure an efficient temperature regulation (p. 118).

In its solvent properties for gases, liquids and solids, water is superior to all other liquids, and for this reason naturally occurring water is never pure. The purest form of naturally occurring water is *rain water*, which has been produced by the condensation, in the upper and cooler regions of the atmosphere, of the water vapour rising from the surface of the earth. Rain water, therefore, has been purified by a process of distillation. In its descent to the earth, however, rain water dissolves not only the normal constituents of the atmosphere—oxygen, nitrogen and carbon dioxide—but also gaseous and other impurities which may be present, more especially in the neighbourhood of towns.

Rain water, after its fall to earth, may penetrate to a greater or less depth, and when it emerges again at the surface as spring water, it will necessarily have become less pure. Its degree of purity or impurity will obviously depend on the length of its course underground and the nature of the materials with which it has come into contact. Sometimes, in the course of its wandering, the water comes into contact with and dissolves substances which give to it characteristic properties, often of medicinal value. In this way are produced different *mineral waters*, which are frequently much sought after and which constitute the chief attraction of many spas and health resorts—alkaline carbonated waters, sulphur waters, chalybeate (iron) waters, etc. The waters of Bath, in Somerset, which have been known since the time of the Romans and to which, led by Beau Nash, fashionable society flocked in the eighteenth century, to get relief from gout and rheumatism, owe their efficacy partly to the presence of radioactive substances.

Spring water passes, in turn, into *river water*, which may dissolve still further quantities of material during its progress to the *sea*, where the amount of dissolved substances—chlorides

and sulphates of sodium, potassium, calcium and magnesium, for the most part—is so considerable as to render the water quite undrinkable. Ocean waters, for example, contain 3–4 per cent. of dissolved solids. Still greater amounts of dissolved material are, however, found in the land-locked lakes, such as the Great Salt Lake, Utah, and the Dead Sea in Palestine, which have no outlet to the sea. Thus the Great Salt Lake contains from 15–23 per cent., and the Dead Sea from 19–26 per cent. of dissolved solids.

**Potable Water.**—Since water is indispensable for life, it is of the highest importance that the supply of water for human consumption should be free from unpleasant or harmful impurity. Drinking water is chiefly derived from rivers or lakes, and the gases and solid matter which are contained in solution—provided they are not present in too large an amount—render the water more palatable.

Formerly, it was considered necessary only to carry out a chemical analysis of water as a proof of its purity, but it is now and has been, indeed, for long, realised that, apart from substances of a poisonous character, *e.g.* lead, the most dangerous impurities are bacterial—disease-producing organisms of typhoid, cholera, etc. Although chemical analysis, by disclosing the presence of excessive amounts of nitrogenous compounds or, of chlorides in the water, can give very valuable indications of contamination by sewage and of the possible presence of pathogenic organisms, only a bacteriological examination can decide whether these organisms are really present or not. Such an examination, therefore, is essential as a safeguard to health.

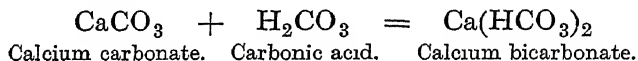
Although filtration through layers of sand and gravel is a very useful process for freeing water from suspended impurities, including bacteria, it is an inadequate treatment in cases where bacterial contamination is large. In some cases, treatment with ozone has been applied in order to destroy micro-organisms, but the substance which is now most widely employed for this purpose, is the gaseous element chlorine, which, even in very minute amount, one or two parts per million, has a powerful germicidal action. Chlorine was first employed near London, in 1889, for the disinfection of sewage, and in 1893 it was applied at Brewster, New York, for the protection of the water supply of New York City. Since that time, its use has greatly extended, and it is to the purification of drinking water by its means that the freedom of the troops from typhoid during the Great War is largely to be attributed. To the chlorination of the water supply, also, the reduction by 79 per cent. of the typhoid death

rate in New York, and by 89 per cent. in Philadelphia, is mainly to be attributed. It is stated that more than three-fourths of the water supplied to cities in the United States for household use, is now treated with chlorine.

In place of the element chlorine one can also use bleaching-powder or sodium hypochlorite (*see later*), substances which are in themselves sources of chlorine.

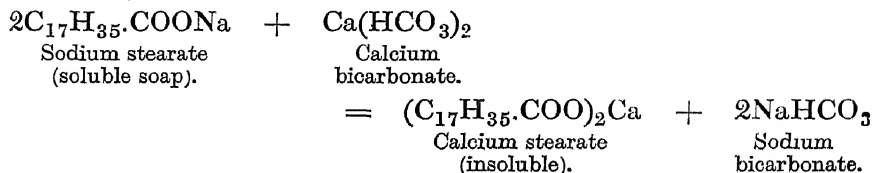
**Hard Water.**—When water, during its course underground, comes into contact with limestone (calcium carbonate,  $\text{CaCO}_3$ ), gypsum (calcium sulphate,  $\text{CaSO}_4$ ) or with magnesium carbonate or sulphate, it dissolves these substances in larger or smaller amount and is thereby rendered “hard,” a term applied to such water because of its feel in washing. Such impurities in water are objectionable and a cause of waste, whether the water be used for domestic or for industrial purposes.

Whereas water dissolves calcium sulphate as such, the calcium and magnesium carbonates are dissolved mainly through the action on them of the carbon dioxide (carbonic acid gas) dissolved in the water. When water containing carbonic acid in solution comes into contact with calcium or magnesium carbonate, the sparingly soluble carbonate is converted into the readily soluble *bicarbonate*, thus :

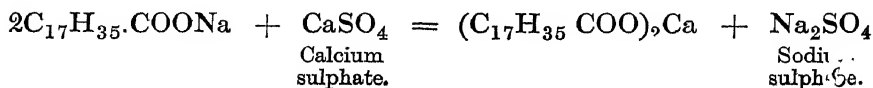


When hard water is used in a kettle or boiler, the dissolved calcium and magnesium compounds separate out and form a hard “scale” or “fur” which insulates the kettle or boiler and so causes a loss of heat. Explosions, moreover, may be caused in boiler tubes owing to the “scale” cracking and so allowing water to come into contact with the overheated tubes.

Hard water, also, when used for washing purposes, is very wasteful of soap, because the calcium and magnesium salts decompose the soap with production of insoluble substances which separate out as a scum. Thus :



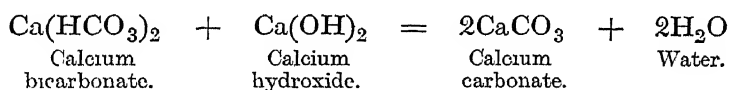
or



Since the soap is thus decomposed, no lather can be obtained and the soap cannot exercise its detergent properties, until sufficient of it has been added to combine with all the calcium and magnesium salts present.

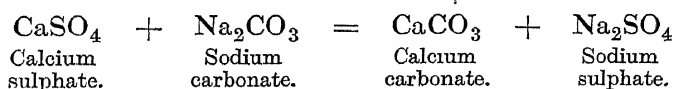
When the hardness of water is due to the presence of bicarbonate of lime, it can be got rid of by boiling, because the bicarbonate is thereby decomposed into the normal carbonate ( $\text{CaCO}_3$ ) and carbonic acid; and this acid, in turn, decomposes into water and carbon dioxide which escapes as a gas. Hardness due to bicarbonates is therefore termed *temporary hardness*. Hardness due to calcium sulphate, however, cannot be removed by boiling, and it is therefore spoken of as *permanent hardness*.

The hardness of water which, whether for its domestic or its industrial use, is very objectionable, can be got rid of, or the water can be *softened*, by various means. Water containing bicarbonates can be softened by the addition of slaked lime (calcium hydroxide) in proper amount. The bicarbonate is thereby converted into normal carbonate and so thrown out of solution :



This water-softening process was first introduced by THOMAS CLARK (1801–1867), Professor of Chemistry in Marischal College and University, Aberdeen.

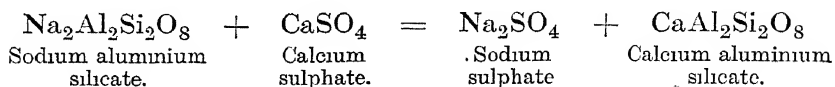
Permanent hardness can be removed by means of soda-ash or sodium carbonate which converts the calcium sulphate in solution into calcium carbonate. The calcium salt is thereby removed from solution and the water softened. Thus :



On this behaviour depends the use of sodium carbonate (“ washing soda ”) in the laundry.

In 1905, another process for the softening of water, known as the *permutit* process, suitable for domestic or industrial use, was introduced. When quartz (silica), alumina and sodium carbonate are fused together, there is formed a sodium aluminium silicate, to which the trade name permutit has been given. When hard water is filtered through a layer of such material, the lime and magnesia (if present) are removed and the water

is thereby rendered soft, the reaction which takes place being represented by the equation :



When the permutit ceases to be effective, its activity can be restored by allowing it to remain for some time in contact with a solution of common salt (sodium chloride), which reconverts the calcium aluminium silicate to sodium aluminium silicate.

**Physical Properties of Water.**—*Pure Water*, which can be obtained by the distillation of naturally occurring water, ordinarily appears as a colourless liquid. When seen through thick layers, as when one views the water of a deep glacier crevasse, it shows a fine blue colour. On being cooled down from the ordinary temperature, water behaves abnormally, in that it diminishes in volume until the temperature of 4° C. is reached, and thereafter it *expands*. To this behaviour is due the fact that lakes do not freeze completely to solid ice, a fact of the greatest importance in the economy of nature.

When, in winter, the temperature falls below the freezing-point, the surface water is first cooled down, and, becoming denser through contraction, it sinks. This process goes on until the whole body of water has been cooled to 4° C. When, however, the surface layers of water are cooled to a lower temperature, expansion takes place, and the water becoming thereby specifically lighter, remains on the surface, and passes, in due course, into ice. Since ice and water are bad conductors of heat, it is only with comparative slowness that the thickness of ice increases. But for this peculiar behaviour of water, lakes and rivers would become converted into solid masses of ice, aquatic life would be destroyed and the conditions of the glacial period would be restored.

Water has a higher *specific heat* than any other liquid ; that is, more heat must be imparted to water in order to raise its temperature by a given amount than has to be imparted to the same weight of any other liquid. For this reason, hot water is a relatively great reservoir of heat, and gives out a large amount of heat on cooling, a fact which finds useful application, on a small scale, in the hot-water bottle. To this property, also, must be attributed the more temperate and equable climate of regions near the sea-coast.

When water at 100° C. is converted into steam at 100°, a large amount of heat—539 calories per gram of water—becomes latent



(p. 120) ; and this heat is again given out when steam condenses to water. For this reason, steam can be used for the transport of a large amount of heat.

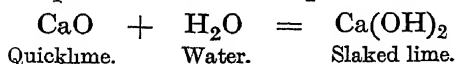
When water passes into ice, expansion amounting to about  $\frac{1}{11}$ th part of the volume of the water takes place ; or 10 volumes of water become 10.9 volumes of ice. For this reason, icebergs float in the sea, although with the greater part of their mass submerged. The bursting of water-pipes, the breaking down of rocks and the opening up of the soil in winter, are familiar consequences of the expansion of water on freezing.

The latent heat of fusion of ice (p. 121) amounts to 79 calories per gram, and is taken advantage of, as has already been pointed out, for the production of low temperatures.

**Composition of Water.**—The composition of water, by weight, was determined with very great care by the American chemist, EDWARD W. MORLEY (1838–1923), Professor of Chemistry at Western Reserve University, Cleveland, Ohio, who published his results in 1895. Morley caused a weighed amount of hydrogen (which was occluded in palladium) to combine with a weighed amount of oxygen in a specially designed tube, and the weight of water produced was also weighed. As the result of a series of most painstaking and exact determinations, Morley found that 2 grams of hydrogen combine with 15.879 grams of oxygen, or 2.016 grams of hydrogen with 16.00 grams of oxygen.

Gay-Lussac, we have seen (p. 105), in collaboration with Alexander von Humboldt, showed, in 1805, that hydrogen and oxygen combine in the ratio of 2 volumes of the former to 1 volume of the latter ; and this result has been confirmed by later and more accurate determinations. This simple volumetric relationship, it will be remembered, inspired Gay-Lussac to investigate other cases of gaseous combination and so led to the discovery of the law of combination of gases by volume associated with the name of this French chemist.

**Some Chemical Properties of Water.**—Although, in some of its chemical reactions, as when it is acted on by sodium or iron, water undergoes decomposition with evolution of hydrogen, yet, in other cases, it may enter into combination with compounds without any loss either of hydrogen or of oxygen. Thus, when water, in not too large an amount, is poured on calcium oxide (quicklime), a considerable amount of heat is evolved, a new compound, *calcium hydroxide*, is produced, and the hard mass of quicklime falls to a powder :



This is, of course, the familiar process known as the *slaking of lime*, and the clouds of steam which are produced are evidence of the vigour of the chemical reaction which takes place.

Similarly, water combines with sodium oxide,  $\text{Na}_2\text{O}$ , to form the compound *sodium hydroxide* or caustic soda ( $\text{NaOH}$ ).

When the slaked lime and the sodium hydroxide are treated with a larger quantity of water, they dissolve—the slaked lime only in small amount—and the solution which is obtained has a soapy feeling and turns a solution of the purple vegetable dye, litmus, *blue*. Substances having this property are called *alkalis*.

On the other hand, when the oxide of phosphorus or of sulphur, for example, is dissolved in water, combination takes place with formation of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), and sulphurous acid ( $\text{H}_2\text{SO}_3$ ), which, as has already been learned (p. 153), turn litmus solution *red*.

One may summarise the results of investigation in the statement that water combines with the oxides of *metals* to form bases (which, if soluble, are called alkalis); and combines with the oxides of *non-metals* to form acids. When an alkali is added to an acid, or an acid to an alkali, the acid and alkaline properties are *neutralised*, and the product of the reaction is termed a *salt*. The nature of these three classes of substances, acids, alkalis and salts, will be considered more fully at a later point.

Water, however, combines not only with the oxides of metals and of non-metals, but it may also combine with salts, which are formed by the interaction of acids and bases. Thus, when zinc and dilute sulphuric acid are brought together, hydrogen is liberated and zinc sulphate is formed (p. 221). This zinc sulphate remains in solution, but if the solution is concentrated by evaporation and then allowed to cool, the zinc sulphate separates out as white crystals. Analysis, however, shows that these crystals have a composition which is represented not by the formula,  $\text{ZnSO}_4$ , but by the formula,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , a compound of 1 molecule of zinc sulphate with 7 molecules of water. Such compounds are known as *salt hydrates*, and this particular compound is called zinc sulphate heptahydrate.<sup>1</sup>

Similar compounds or hydrates are formed with many other, but by no means with all salts, and some of the hydrates are familiar to all. Copper sulphate, for example, forms with water the hydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , or copper sulphate pentahydrate, the beautiful, blue-coloured, crystalline salt known as *bluestone*. When this hydrate is heated, the *water of hydration*, as it is

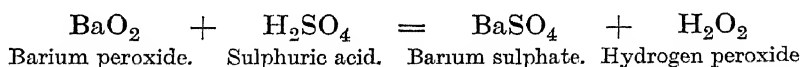
<sup>1</sup> From the Greek *ἑπτά* (*hepta*), seven.

called,<sup>1</sup> passes off as water vapour, and one obtains the *anhydrous*<sup>2</sup> copper sulphate,  $\text{CuSO}_4$ , in the form of a white crystalline powder. On bringing this into contact with water, hydration takes place with evolution of heat and formation of the blue pentahydrate.

Salt hydrates exhibit a vapour pressure which increases with rise of temperature. Even at the ordinary temperature, the vapour pressure may, in some cases, exceed the pressure of the water vapour in the air. In such cases, the salt hydrate, when exposed to the air, will lose its water of hydration, in whole or in part, and pass either into the anhydrous salt or into a lower hydrate. Since this process is generally accompanied by a change of crystalline form and a crumbling of the hydrate to a powder, it is spoken of as *efflorescence*. This phenomenon is well shown by the familiar substance, washing-soda or sodium carbonate decahydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). At the ordinary temperature, the vapour pressure of this compound is higher than the normal pressure of the water vapour in the air, and, consequently, when the hydrate is left exposed to the air, water vapour passes off and the hydrate crumbles to a powder of the monohydrate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ .

### HYDROGEN PEROXIDE

By the action of cold dilute sulphuric acid on a substance known as barium peroxide, the compound known as hydrogen peroxide is formed :



A solution is thus obtained which can be concentrated by distillation under reduced pressure. In dilute solution, hydrogen peroxide is fairly stable; but if the solution is made alkaline, decomposition readily occurs, and this decomposition may be markedly accelerated by the presence of platinum and other substances, as will be discussed more fully at a later point.

Owing to the readiness with which hydrogen peroxide decomposes into water and oxygen, it acts as an oxidising agent. As such it finds application as a mild bleaching agent for silk, ivory, etc. It is also used as a disinfectant and bactericide, for the removal of pus and as a mouth wash. Its use for cleaning and restoring old paintings depends on the fact that it oxidises

<sup>1</sup> It is also sometimes, but less properly, called "water of crystallisation."

<sup>2</sup> From the Greek  $\alpha$  (alpha), not, and  $\nu\delta\omega\rho$  (hydōr), water.

the black lead sulphide ( $\text{PbS}$ ), which is formed by the action of sulphur vapours on the "white lead" present in the pigments, to white lead sulphate ( $\text{PbSO}_4$ ).

Analysis shows that while 8 parts by weight of oxygen are combined with 1.008 parts by weight of hydrogen to form water, in hydrogen peroxide 16 parts by weight of oxygen are combined with 1.008 parts by weight of hydrogen. This is in harmony with the law of multiple proportions discovered by Dalton (p. 57).

Since, in hydrogen peroxide, hydrogen and oxygen are combined in the proportions of 1.008 parts of the former to 16.0 parts of the latter, it follows that the empirical formula (p. 137) is  $\text{HO}$ . The method by which the molecular weight of hydrogen peroxide has been determined and the true formula of the compound shown to be  $\text{H}_2\text{O}_2$ , will be discussed in the next chapter.

## CHAPTER XV

### SOLUTIONS

**What is a Solution ?**—When one brings sugar, salt, washing-soda, and many other common and familiar substances into contact with water, the solid substance, if present in not too large amount, disappears; it *dissolves*, and a clear liquid is obtained which is called a *solution*. Although, doubtless, in some cases, combination of the dissolved substance, or *solute*, with the solvent takes place, one must not regard the solution as a whole as being a compound of water (or the solvent), with the sugar, salt or other dissolved substance. A compound is characterised, as we have already seen, by the fact that its composition is perfectly definite and constant, and cannot be altered by adding more or less of one of the constituents. The composition of a solution, however, can be altered as we please, within certain limits; and the proportions in which the solute and solvent are present in the solution may be varied, in some cases varied very greatly, so that one obtains solutions of different strength or *concentration*. Even if chemical combination does take place, it appears to do so only to a limited extent, and is accompanied by a mechanical intermingling of the molecules. One may, therefore, regard a solution as being merely a homogeneous mixture in which the molecules of the dissolved substance or solute, combined, it may be, with a limited number of solvent molecules, are uniformly distributed throughout and among the molecules of the water, or other liquid which acts as the solvent. *A solution, in short, is a homogeneous mixture of variable composition.*

Restricting the present discussion to solutions in which water is the solvent,<sup>1</sup> it is clear that homogeneous mixtures may be obtained not only with solids, like cane sugar, but also with gases and with liquids. Except in the case of liquids under certain conditions, to be considered later, water can dissolve only a limited or restricted amount of the solute. Thus, when a gas or a solid is kept in contact with water, solution takes

<sup>1</sup> The discussions would not be essentially different for other liquids as solvents.

place, and the process continues only until the concentration of the solute reaches a definite value, which is independent of the amount of gas or solid present, so long as these are present in excess—a fact well known even in the days of Pliny. A condition of *equilibrium* is established between the gas and the solution or between the solid and the solution; and when the solution is in this state of equilibrium, it is said to be *saturated*. The concentration of the solute in the saturated solution, or the amount of solute in a definite amount of solvent, is called the *solubility* of the solute in the particular solvent, and may be expressed in various units.

**Solubility of Gases.**—When water is shaken with a gas, such as oxygen or carbon dioxide, the amount of gas which dissolves is found to depend not only on the temperature but, very markedly, also on the pressure. The solubility, or the amount of gas by weight which dissolves in a given amount of water, decreases with rise of temperature and increases with increase of pressure; and the relation between the solubility and the pressure is summed up in the law enunciated in 1803 by the English chemist, WILLIAM HENRY (1775–1836), and known as HENRY'S LAW. This law states that “under equal circumstances of temperature, water takes up in all cases the same *volume* of condensed gas as of gas under ordinary pressure”; or, the *volume* of a gas dissolved by a given amount of water at a given temperature, is independent of the pressure. Since, on the basis of Boyle's law, the amount of a gas contained in a given volume is proportional to the pressure, Henry's law may also be stated in the form: The *amount* of a gas dissolved by a given amount of water at a given temperature is proportional to the pressure. The law, however, is not valid for very soluble gases, such as ammonia or hydrogen chloride.

In the preparation of aerated beverages, first produced artificially by Priestley, carbon dioxide is pumped into water under pressure, or the carbon dioxide is formed under pressure by fermentation (as in the case of beer), and consequently, the amount of gas dissolved is greater than if the water were shaken with carbon dioxide under atmospheric pressure. When, therefore, the bottle containing the beverage is opened, carbon dioxide escapes with effervescence, so as to reduce the concentration of gas in the liquid to that which is in equilibrium with the gas under atmospheric pressure. Although there is, at first, a sudden rush of gas when the pressure is reduced, later, the gas escapes from solution and the condition of equilibrium is approached only slowly, if the liquid is left undisturbed. The

solution tends to remain *supersaturated*. If, however, the solution be shaken or if bubbles of air be passed through the solution, the so-called *metastable equilibrium* of the supersaturated solution is upset and the excess of gas rapidly escapes. The vigorous effervescence which takes place on dropping a piece of bread or a spoonful of sugar—the particles of which carry air in their pores or are coated with a film of air—into a glass of comparatively quiescent beer or other aerated beverage, is probably familiar to all.

**Solubility of Liquids.**—The solubility of a liquid in water at any given temperature may be infinite or it may be limited. Thus, as is well known, if alcohol (spirits of wine) be added to water, the two liquids mix completely in all proportions. Alcohol and water are completely miscible with each other. On the other hand, if ether and water, or phenol (carbolic acid) and water, be shaken together, it will be found that a given amount of water can dissolve only a limited amount of ether or of phenol. In the case of liquids, moreover, solubility is mutual, and so it is found that just as water dissolves a limited amount of ether or of phenol, so ether and phenol dissolve a limited amount of water. If, then, a quantity of water is shaken with, say, excess of phenol, a white emulsion is formed which, on standing, rapidly separates into two liquid layers; a lower layer, consisting of a saturated solution of water in phenol, and an upper layer, consisting of a saturated solution of phenol in water.

The mutual solubility of liquids, however, alters with the temperature, and it is found, in the case of phenol and water, for example, that the mutual solubility increases with rise of temperature. As the temperature is raised, therefore, the composition of the two mutually saturated solutions becomes more nearly the same, until, at about 66° C., the two liquid layers become identical in composition. That is to say, the two liquid layers pass into a single homogeneous solution. The temperature at which this takes place is called the *critical solution temperature*. At temperatures above the critical solution temperature, the liquids are miscible in all proportions.

If to the mixture of water and phenol one adds a third substance, the temperature at which a single homogeneous solution is formed is greatly altered. If the substance added is soluble in both water and phenol, the mutual solubility is increased and the temperature at which these two substances become completely miscible, is lowered. This fact is made use of in the preparation of concentrated antiseptic liquids, such as Lysol, Jeyes' fluid, etc., which are produced by the addition of

sodium oleate (a soap) to mixtures of water and phenol or water and cresol, a substance which is related to phenol. By the addition of sodium oleate, the critical solution temperature is lowered to below the ordinary temperature, and solutions may therefore be prepared containing as large a proportion as may be desired of phenol or of cresol.

**Solubility of Solids.**—The condition of equilibrium which is established between a solid and a solution, that is, the solubility of a solid, depends not only on the nature of the solid substance but also on the temperature. Little is known regarding any general relation between chemical composition and solubility; and with regard to the influence of temperature on the solubility, a very diverse behaviour is found. This will be obvious from an examination of the solubility curves shown in Fig. 49. In some cases, *e.g.* sodium chloride, the solubility varies only slightly with the temperature, but in other cases, *e.g.* potassium nitrate, very great variation is shown. Sometimes the solubility diminishes with rise of temperature; and the solubility curve may also show a maximum or a minimum point.

On examining Fig. 49, it will be observed that the solubility curve for sodium sulphate differs markedly from the other curves, for in this case the curve shows, at about  $33^{\circ}$  C., a *sudden* change in direction. The curve is no longer continuous. This behaviour, which is very important, is a sure indication that a change takes place in the nature of the solid substance in contact with the solution; and when one investigates the matter more closely, it is found that up to a temperature of  $33^{\circ}$ , the solid which is in contact with the solution is Glauber's salt or hydrated sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , whereas the solid in contact with the solution above  $33^{\circ}$ , is the anhydrous salt,  $\text{Na}_2\text{SO}_4$ . One is really dealing, therefore, not with one solubility curve but with two solubility curves—that for the hydrated and that for the anhydrous salt. Above  $33^{\circ}$ , Glauber's salt is not stable, even in contact with aqueous solution, but loses its water of hydration and passes into the anhydrous salt. Below  $33^{\circ}$ , on the other hand, anhydrous sodium sulphate, in presence of water, passes into the hydrated salt. For this reason, *anhydrous* sodium sulphate may be used for the purpose of drying or removing small quantities of water from liquids at temperatures below  $33^{\circ}$ .

If the saturated solution of a solid, the solubility of which increases with the temperature, is prepared at some temperature above the ordinary and is then cooled down, out of contact with the solid, crystallisation of the excess of solute may not take



place. The solution is then said to be *supersaturated*. With proper precautions, a supersaturated solution may be preserved

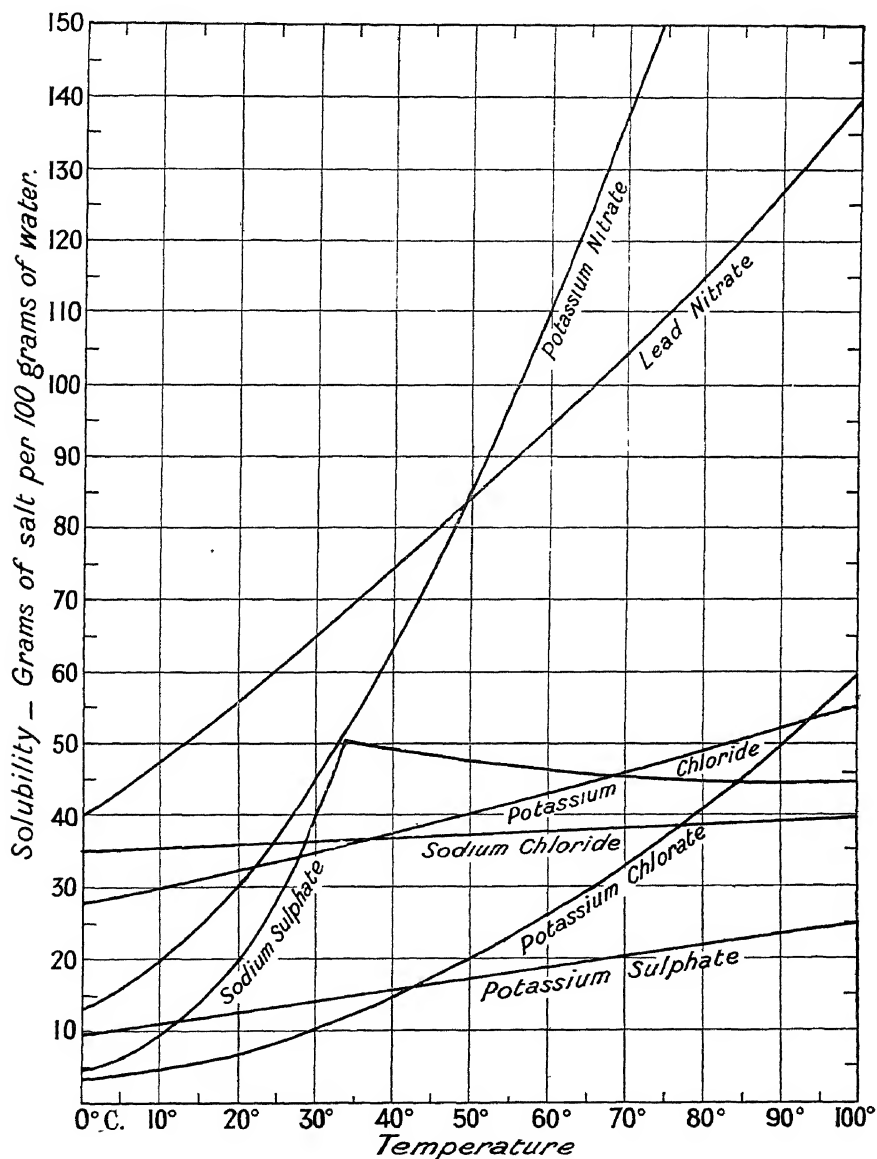


FIG. 49.—Solubility of salts in water.

indefinitely, provided that all traces of the crystalline solid are rigidly excluded. If, however, a minute trace, even the ten

thousand millionth part of a gram, of the solid substance—a particle which might float in the air as a speck of dust—is brought into contact with the supersaturated solution, the state of apparent equilibrium—a so-called *metastable* equilibrium—is upset, the solute begins to crystallise out, and the process continues until the concentration in the solution becomes equal to the solubility value at the particular temperature.

This behaviour may readily be demonstrated by preparing a saturated solution of sodium sulphate at a temperature of say 50° C. At this temperature the sodium sulphate is anhydrous and 100 grams of water dissolve about 50 grams of the sulphate,  $\text{Na}_2\text{SO}_4$ . If the solution is then carefully separated by filtration from all particles of the solid, and cooled down to the room temperature (15°),<sup>1</sup> no crystallisation takes place although, at this temperature, a saturated solution of hydrated sodium sulphate contains only about 13 grams of the salt to 100 grams of water. If even a minute crystal of Glauber's salt or hydrated sodium sulphate<sup>2</sup> ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) be dropped into the solution, crystallisation begins at once.

**Purification by Recrystallisation.**—Owing to the great differences which exist between the solubilities of different substances, as well as to the variation of the solubility with temperature, it is possible, by crystallisation, to separate one solid from another with which it may be mixed, and so to purify it. Thus, if a mixture of 30 grams of potassium chlorate and 30 grams of the yellow salt, potassium chromate, is dissolved in 100 grams of hot water, and the solution then allowed to cool to room temperature, about 24 grams of potassium chlorate will crystallise out, because the solubility of this salt at 15° C. is only about 6 grams per 100 grams of water. Since, however, more than 60 grams of potassium chromate dissolve in 100 grams of water at 15°, none of the potassium chromate will separate from the mixed solution. The crystallised potassium chlorate is separated from the solution by filtration, and washed free from the *mother liquor*, with a small quantity of cold water. This method of *recrystallisation*, as it is called, is very frequently made use of for the purification of crystalline solids.

**Diffusion and Osmotic Pressure.**—In discussing the properties of the gaseous state, it was pointed out that a gas, owing to the molecules being in rapid motion, can diffuse or distribute

<sup>1</sup> As particles of sodium sulphate may be present in the dust of the air, the mouth of the vessel should be closed by a plug of cotton wool.

<sup>2</sup> Sodium sulphate crystallises from water at the ordinary temperature, as hydrated salt.

itself uniformly throughout the whole space offered to it no matter how large that space may be. In the case of liquids, we have seen, the molecules are also in motion; and they possess, therefore, the power of diffusion. The process, however, now takes place more slowly, for the molecules of the liquid are packed more closely together, and the mutual collisions are therefore more frequent. The forward progress of a molecule is, in consequence, very slow, like that of a man who might try to pass through a dense and jostling crowd. Nevertheless, diffusion does take place, as we can easily satisfy ourselves by carefully bringing a layer of water on the top of a concentrated solution of a coloured substance (*e.g.* copper sulphate or potassium permanganate), standing at the bottom of a cylinder. In the course of time it will be found that the coloured solute has diffused upwards into the water, while, at the same time, water will have diffused downwards into the solution. The experiment can be carried out more easily by pouring the coloured solution<sup>1</sup> into a test-tube which is two-thirds filled with a 3 per cent. gelatine jelly. After a time, it will be found, the coloured solute will have diffused some distance into the gelatine jelly.

Even when the solution is separated from the pure water by a membrane of parchment paper, diffusion takes place just the same, as can be shown by placing a solution of copper sulphate in a parchment tube or "thimble," which is then immersed in water. Very soon it will be possible to detect the presence of copper sulphate in the water outside the tube.

Further interesting information concerning the process of diffusion, which takes place because the solvent and solution are not in equilibrium with each other, is obtained if one attaches the parchment "thimble" firmly to a glass tube as shown in Fig. 50. A concentrated solution, say, of cane sugar, is poured through the side-tube *a* until the level rises to a point in the narrow glass tube. The parchment tube is then immersed in pure water. After some time, it will be found that the level of the solution has risen, thereby producing a hydrostatic pressure in the parchment tube. The production of such a pressure, first observed, in



FIG. 50.—Osmotic pressure.

<sup>1</sup> For this experiment the deep-blue coloured solution obtained by adding ammonium hydroxide to a solution of copper sulphate is very suitable.

1748, by the French *Abbé*, JEAN ANTOINE NOLLET (1700–1770), a Professor of Physics in Paris, indicates that water molecules diffuse through the parchment membrane more rapidly than solute molecules do; and since the pressure is produced by a process known as *osmosis*,<sup>1</sup> or diffusion of a liquid through a membrane, it has been called an osmotic pressure. Since the membrane of parchment paper is permeable to the sugar molecules as well as to the molecules of water, the hydrostatic pressure or osmotic pressure cannot be permanent; and the level of the liquid in the osmometer—as the apparatus may be called—after rising to a certain maximum height, will fall until the level of liquid outside and inside the osmometer is the same. This will occur when, through osmosis, uniform concentration of solution has been established throughout the liquid inside and outside the osmometer.

Since the osmotic pressure produced in the experiment just described is due to a difference in the *relative* velocity of osmosis of solvent and solute molecules, it is clear that in proportion as the membrane becomes relatively less and less readily permeable to the solute, the observed pressure will increase. It is, however, possible to imagine a membrane which, while still permeable to water molecules, is quite impermeable to solute molecules; and with such a membrane—called a *semipermeable membrane*—osmosis can, of course, take place only in one direction, namely, inflow of water to the solution. The process of osmosis, however, cannot go on indefinitely, for, as the hydrostatic pressure inside the osmometer increases, or as the pressure on the solution increases, it tends to force the solvent back again through the membrane. That is to say, the mechanical or hydrostatic pressure produced by the osmosis of water into the solution opposes the force causing the osmosis; and when the two become equal, osmosis will stop. The hydrostatic or osmotic pressure produced with such a membrane as has been here postulated, is an *equilibrium pressure*, and is no longer temporary but permanent; and the pressure so produced is the *maximum* pressure which can be attained with the given solution. This maximum pressure, obtained with a semipermeable membrane, is now generally referred to as *the osmotic pressure of the solution*.

It will be clear that this conception of the osmotic pressure of a solution will have no real value, for one will not be able to measure it, unless it is possible to obtain a semipermeable membrane. Fortunately, such a membrane can be obtained, semipermeable for certain solutions at least, for it has been found that

From the Greek *ὄσμος* (*ōsmos*), a push.

a membrane of copper ferrocyanide will allow water molecules to pass through but not the molecules of cane sugar.

**Measurement of Osmotic Pressure.**—In attempting to use such a membrane for the construction of an osmometer, or apparatus for the measurement of osmotic pressure, the difficulty is at once encountered that the membrane is much too weak to withstand the pressures which are produced, amounting, as they do in some cases, to many atmospheres. This difficulty was, however, surmounted in 1877 by WILHELM PFEFFER (1845–1920), Privatdozent in Bonn, and later Professor of Botany in the Universities of Tübingen and of Leipzig, who filled a battery pot of porous ware with a solution of copper sulphate and then stood it in a solution of potassium ferrocyanide. Diffusion of the salts took place, and where the two salts met in the walls of the pot, a gelatinous precipitate of copper ferrocyanide was formed. The precipitate so obtained, being supported by the material of the pot, was found capable of sustaining considerable pressures.

A sketch of the apparatus, ready for use, is shown in Fig. 51. The porous pot, *z*, containing the solution of which the osmotic pressure is to be measured, is connected with a closed manometer, *m*, by means of the tube, *t*, and the collars, *v* and *r*. The pot is then placed in pure water kept at constant temperature. In the course of a short time the pressure inside the pot is shown by the manometer to increase, and ultimately to become constant. The constant pressure thus produced represents the osmotic pressure of the solution.

With this apparatus a number of determinations of osmotic pressure were made by Pfeffer, who found that the osmotic pressure is proportional to the concentration of the solution, and that it increases with rise of temperature.

The study of osmotic phenomena has, primarily, a great biological interest, because of the fact that plant and animal cells are surrounded by a quasi-semipermeable membrane, or a membrane which possesses the property of selective permeability, of such a kind that it is capable of allowing the passage of water and of certain dissolved substances while it retains soluble food-stuffs within the cell.

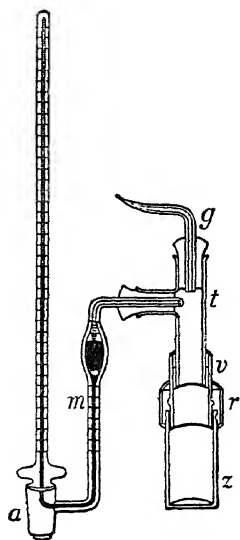


FIG. 51.—Pfeffer's osmometer.

When a plant cell is immersed in a solution which is more concentrated than that of the cell contents, water passes *from* the cell into the outer solution. The cell, therefore, contracts away from its supporting cellulose framework (Fig. 52, B and C), and thereby loses its *turgor* or tenseness. If, however, the cell

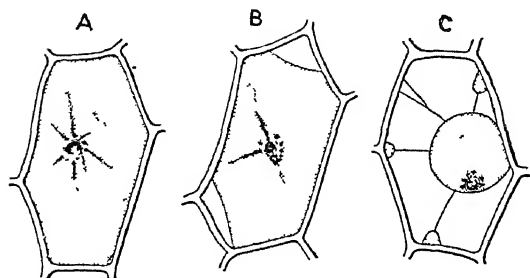


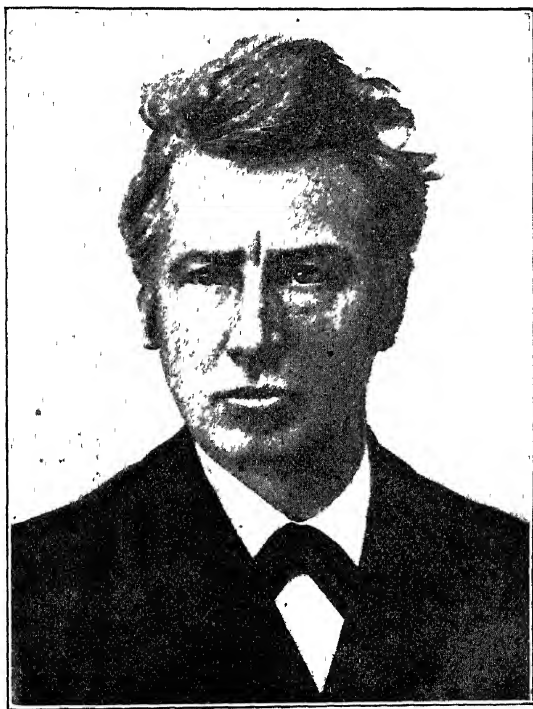
FIG. 52.—Osmotic pressure and plant cells.

the cell sap, water passes *into* the cell. A pressure is created within the cell which thereby regains the turgor or "tone" necessary for healthy life, and presses against its cellulose support (Fig. 52, A). One can understand, therefore, why a plant which has wilted owing to loss of water by evaporation or because the salt concentration of the solution entering through the roots is too high, can be revived by placing in pure water. In the life of animal cells, also, osmotic pressure plays an important part.

The phenomena of osmotic pressure, however, possess an interest and importance not only for the biologist but also for the chemist and physicist, and the study of these phenomena led van't Hoff, in 1886, to the discovery of a very important analogy between substances in the gaseous state and in dilute solution, an analogy which finds expression in the words: *A substance in dilute solution behaves as if it were a gas occupying the volume of the solution and under a pressure equal to the osmotic pressure.*

JACOBUS HENRICUS VAN'T HOFF, pre-eminent for his contributions to theoretical chemistry, and acclaimed during his life as "the greatest living physical chemist," was born at Rotterdam in August 1852. At the age of seventeen, he entered the Polytechnic at Delft for the purpose of qualifying as an engineer, but before he had completed his course, he had decided to devote himself to chemistry, a subject to which he had taken a liking even while at school. Attracted by the work of the great German chemist Kekulé, van't Hoff proceeded to the University of Bonn in 1872, and there his first experimental investigations were carried out. It was not, however, through laborious experimental investigations that van't Hoff was to attain his undying fame. His was a mind which found no satisfaction in acquiring an

encyclopædic knowledge of details, but one which strove to gain a knowledge of fundamentals; a generalising and speculative mind which worked in a poetic sphere in which his scientific imagination sought to "seize truth as it were by anticipation." The first fruit of van't Hoff's habit of speculating and daydreaming, noticeable even in his school-days, is to be found in his epoch-making theory of the "asymmetric carbon atom" which forms the foundation of stereochemistry (see Chap. XXVIII),



JACOBUS HENRICUS VAN'T HOFF.

and which was published in 1874. At that time, van't Hoff was just 22 years old! Important as was his *Chemistry in Space*, his *Studies in Chemical Dynamics*, first published in French in 1884, was still more important. In this work—one of the great classics of chemical science—van't Hoff placed the study of the velocity of chemical reactions, chemical affinity and chemical equilibrium on a firm basis of thermodynamics, and through his interest in these fundamentally important questions he was led to the discovery of that analogy between substances

in the gaseous state and in solution to which reference has been made above.

In 1896, van't Hoff left Amsterdam for Berlin, having accepted election to the Academy there and appointment as an Honorary Professor in the University; and in Berlin he remained for the rest of his life, unravelling, with the help of graduate students from different countries of the world, the solubility relations and the conditions of formation and separation of the salts of the great Stassfurt deposits.

Although honours were showered upon him by Universities and learned Societies, and included the award, in 1901, of the first Nobel Prize in Chemistry, van't Hoff retained throughout the kindness of heart and the quiet simplicity of character which had marked his whole life and which added a glory to his genius.

Attacked by tuberculosis, van't Hoff died on March 1st, 1911.

**Analogy between Solutions and Gases.**—On the basis of thermodynamics and by employing the conception of a semi-permeable membrane, van't Hoff deduced that the osmotic pressure of a dilute solution is proportional to the concentration and to the absolute temperature, two laws which are obviously the analogues of the laws of Boyle and of Gay-Lussac for gases, and which were confirmed by the measurements of Pfeffer. He deduced, moreover, the law that solutions which contain the same number of gram-molecules of solute in a given volume of solution, have the same osmotic pressure, just as gases which contain the same number of gram-molecules in a given volume, exercise the same gaseous pressure. For 1 gram-molecule of a gas, we have seen, the relationship between pressure, volume and absolute temperature is, for all gases, given by the equation  $pv=RT$ ; and, for 1 gram-molecule of a substance in solution, there obtains the analogous equation,  $PV=KT$ , where  $P$  is the osmotic pressure and  $V$  the volume of the solution. Still more surprising, however—and here the analogy is completed—the constant  $K$  for solutions has the same value as the constant  $R$  for gases.

By his discovery of the analogy between substances in dilute solution and gases, van't Hoff laid the basis of a theory of solutions which, although applicable only to dilute solutions, has, by reason of its simplicity, exercised an extraordinary influence on the development of physical, chemical and biological science. The more recent and exact measurements of osmotic pressure carried out by H. N. MORSE (1848–1920) and co-workers



at Johns Hopkins University, Baltimore, and by the EARL OF BERKELEY and E. G. J. HARTLEY in England, have shown, however, that in concentrated solutions the simple laws of osmotic pressure enunciated by van't Hoff are no longer valid.

On the basis of the analogy discovered by van't Hoff, it is possible to determine the molecular weight of substances in solution from determinations of the osmotic pressure, just as one can determine the molecular weight of a substance in the gaseous state from determinations of the vapour density. Thus, we have seen that 1 gram-molecule of a substance in the gaseous state, when occupying a volume of 22.4 litres at 0° C., will exercise a pressure of 1 atm. (76 cm. of mercury). Consequently, we can say, 1 gram-molecule of a solute in 22.4 litres of solution will have, at 0° C., an osmotic pressure of 1 atm. or 76 cm. of mercury. On the basis of this relation, the molecular weight of a dissolved substance can be calculated, as is shown by the following example, taken from the determinations of osmotic pressure by Pfeffer.

A solution containing 1 gram of cane sugar in 100.6 c.c., was found to have an osmotic pressure at 0° C. of 49.3 cm. of mercury. From this one can calculate how many grams of cane sugar would have to be dissolved in 22.4 litres of solution, in order to produce an osmotic pressure of 76 cm. of mercury.

Thus: 1 gram in 100.6 c.c. =  $\frac{1 \times 22,400}{100.6} = 222.6$  grams in 22,400 c.c.

Since the osmotic pressure is proportional to the concentration,

a solution containing  $\frac{222.6 \times 76}{49.3} = 343$  grams in 22,400 c.c.,

will have an osmotic pressure at 0° of 76 cm. of mercury. The number 343, therefore, represents the approximate molecular weight of cane sugar. The value corresponding to the formula  $C_{12}H_{22}O_{11}$  is 342.

**Freezing-point of Solutions.**—Owing to manipulative difficulties and the impossibility of obtaining membranes which are semipermeable for all the different solutes, determinations of the osmotic pressure are not a satisfactory means of ascertaining the molecular weights of substances in solution. Fortunately, however, as van't Hoff pointed out, there is an intimate connection between the value of the osmotic pressure of a solution and its freezing-point. It had long been known that when a substance is dissolved in water, the freezing-point of the water is thereby lowered; and, even in 1883, it was shown by FRANÇOIS MARIE RAOULT (1830–1901), Professor of Chemistry in the University of Grenoble, that *the depression of the freezing-point is proportional to the molecular concentration of the solution.*

Consequently, all aqueous solutions containing the same number of gram-molecules of solute in a given amount of solvent freeze at the same temperature. Knowing that 1 gram-molecule of a solute dissolved in 1000 grams of water gives a solution which freezes at  $-1.86^{\circ}\text{C}$ ., it becomes possible, from determinations of the freezing-point<sup>1</sup> of aqueous solutions, to calculate the molecular weight of the solute. Thus :

0.18 gram of hydrogen peroxide dissolved in 17.61 grams of water gave a solution which froze at  $-0.571^{\circ}\text{C}$ . What is the molecular weight of hydrogen peroxide ?

The concentration of the solution is such that there are  $\frac{0.18 \times 1000}{17.61} = 10.23$  grams of hydrogen peroxide to 1000 grams

of water. This concentration of solute, however, gives a depression of the freezing-point of only  $0.571^{\circ}$ . Therefore, the concentration necessary to give a depression of  $1.86^{\circ}$  is  $\frac{10.23 \times 1.86}{0.571}$

$= 33.3$  grams per 1000 grams of water. The number 33.3, therefore, represents the approximate molecular weight of hydrogen peroxide. Since the empirical formula of hydrogen peroxide is  $\text{HO}$ , the multiple of this which has a molecular weight nearest to 33 is  $\text{H}_2\text{O}_2$ , the molecular weight of which is 34.03. This formula, therefore, is the true formula of hydrogen peroxide.

**Boiling-point of Solutions.**—Whereas the freezing-point of a solution is lower than the freezing-point of the pure solvent, the boiling-point is higher ; and it has been found that *the elevation of the boiling-point is proportional to the molecular concentration of the solution*. In the case of aqueous solutions, it has been found that when 1 gram-molecule of solute is dissolved in 1000 grams of water, the boiling-point, under atmospheric pressure, is  $100.52^{\circ}\text{C}$ . That is, the “molecular elevation” of the boiling-point is  $0.52^{\circ}\text{C}$ . From determinations of the boiling point of a solution, therefore, one can also calculate the molecular weight of a dissolved substance.

It will be very obvious that the properties of solutions which have just been discussed, and more especially the laws connecting the concentration of a solution with the depression of the freezing-point and elevation of the boiling-point of the solvent, are of the highest practical as well as theoretical importance ; for on these laws there have been based methods by which it is possible to determine the molecular weight of substances, such as hydrogen peroxide, which cannot be obtained in the state of gas or vapour.

<sup>1</sup> These are known as *cryoscopic* determinations, this term being derived from the Greek *κρύος* (kryos), frost, and *σκοπεῖν* (skopein), to observe.

It must, however, now be emphasised that the laws which have been discussed in the preceding pages do not apply, in their simple form, to all solutes. They apply to substances such as cane sugar, glycerin and alcohol, but they do not apply to the large groups of compounds known generally as acids, alkalis and salts. The reason for this will be discussed in the following chapter.

## CHAPTER XVI

### ACIDS, ALKALIS AND SALTS. THEORY OF IONISATION

**Abnormal Behaviour of Solutions.**—The simple laws of van't Hoff and of Raoult do not, as has just been stated, apply without modification to solutions of those substances which are known as acids, alkalis and salts. An aqueous solution of cane sugar or of glycerol (glycerin<sup>1</sup>), containing 0.20 gram-molecule of solute in 1 litre of solution (strictly, 1000 gm. of solvent), freezes at  $-0.186^{\circ} \times 2 = -0.372^{\circ}$  C. (p. 246), and it might therefore be expected that a solution of common salt (sodium chloride) containing 0.20 gram-molecule of solute in 1 litre of solution, would also freeze at  $-0.372^{\circ}$ . Experiment, however, shows that this is not the case. The solution of sodium chloride freezes at  $-0.693^{\circ}$ ; or, the depression of the freezing-point of the salt solution is greater than that of the sugar solution of the same

molecular concentration, in the ratio  $\frac{0.693}{0.372} = 1.863$ . In other words, the solution of sodium chloride behaves cryoscopically as if it had a concentration of  $0.20 \times 1.863 = 0.372$  gram-molecule per litre.

Not only do solutions of salt show an abnormal cryoscopic behaviour, but the behaviour is all the more abnormal the more dilute the solution. Thus, when the solution of sodium chloride contains only 0.117 gram-molecule per litre, the depression of the freezing-point is 1.93 times greater than for a solution of cane sugar of the same molecular concentration; and when the concentration is reduced to 0.047 gram-molecule per litre, the depression is twice as great. Different salts, moreover, show different degrees of abnormality, sometimes greater, sometimes less, than that shown by solutions of sodium chloride. In all cases, however, the solutions behave *as if* they contained an abnormally large number of molecules or solute particles in solution; that is to say, they behave *as if* the molecules of the

<sup>1</sup> The systematic name of the substance is glycerol, but the older name glycerin is popularly used.

salt broke up in solution so as to yield a larger number of particles, each of which behaves as a separate solute molecule.

It is worthy of note that in the case of certain substances in the gaseous state, a closely analogous phenomenon is observed. It is well known, for example, that when ammonium chloride ( $\text{NH}_4\text{Cl}$ ) is vaporised by heat, the molecules of the compound, in the vapour state, undergo *dissociation* with production of molecules of ammonia ( $\text{NH}_3$ ) and of hydrogen chloride ( $\text{HCl}$ ). In the vapour, therefore, there are present not only molecules of  $\text{NH}_4\text{Cl}$ , but also molecules of  $\text{NH}_3$  and  $\text{HCl}$ . Consequently, one finds that when a given quantity of ammonium chloride is vaporised in an exhausted vessel, the pressure produced is greater than the pressure which would be produced in the same vessel by an equimolecular amount of hydrogen at the same temperature. In other words, the behaviour of ammonium chloride in the state of vapour does not appear to be in harmony with Avogadro's theorem. Certain other substances behave in a similar manner.

Just as the apparently abnormal behaviour of ammonium chloride in the vapour state finds its explanation in the dissociation of the molecules, so one may assume that when salts, acids and alkalis are dissolved in water, they also dissociate; for their solutions behave as if the number of dissolved molecules were greater than that calculated from the simplest molecular formula of the dissolved compound. If, however, one makes this assumption, the question at once arises: What, then, are the products of dissociation? Into what, for example, does sodium chloride dissociate when it is dissolved in water? Clearly, not into sodium and chlorine; for sodium is a metal which decomposes water with evolution of hydrogen, and chlorine is a gas which dissolves in water, imparting to it a characteristic odour and bleaching properties. An answer to the question was found from a study of the behaviour of solutions towards electricity.

**Electrolytes and Non-electrolytes.**—When one places in a vessel containing pure distilled water, the ends of two wires which are connected with an electric-lighting circuit and lamp (Fig. 53), the lamp remains dark. The electrical circuit is broken by the water, which is a non-conductor of electricity. If to the water one adds cane sugar, glycerin, or alcohol, the lamp still gives forth no light, for the solutions of these substances do not conduct the electric current. When, however, one dissolves in the water even a very little common salt, or caustic soda, or hydrochloric acid (spirit of salt, as it is frequently called), the lamp at once lights up, showing that the flow of electricity is no

longer interrupted by the liquid. In the same way, other substances soluble in water may be tested, and it will be found that the different substances can be divided into two classes, those that yield solutions which conduct electricity, and those that yield solutions which do not conduct electricity. Substances belonging to the former class are called *electrolytes*, substances belonging to the latter class, *non-electrolytes*. Sugar is a non-electrolyte; salt is an electrolyte. Similarly, all the substances known as *acids*, which have a sour taste and the property of turning red a blue solution of the vegetable colouring matter called litmus; all the substances, also, known as *alkalis*, which have the opposite property of restoring the blue colour to solutions of litmus which have been reddened by acids; and lastly, all the substances known as *salts*, which are formed by the com-

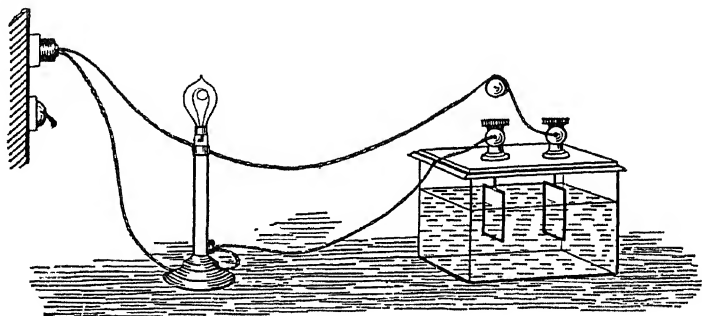


FIG. 53.—Conductivity of solutions for electricity.

bination of acids and alkalis; all these substances, acids, alkalis and salts, are electrolytes, and yield solutions which conduct the electric current.

When an electric current is passed through the solution of an electrolyte, even the most superficial observation will teach us that a liquid conductor differs from a metallic one. In the latter case, no apparent change takes place, but in the former, there is a very obvious decomposition of the conducting solution. This process of decomposition by an electric current is known as *electrolysis*,<sup>1</sup> and has already been employed for the production of hydrogen and oxygen (p. 222). A similar decomposition is observed when one passes a current of electricity through, or *electrolyses*, a solution of copper sulphate. In this case, it is observed that the surface of one of the *electrodes* (as the portions of the metallic conductor dipping into the solution are called),

<sup>1</sup> From the stem of the word electricity and the Greek word λύσις (lysis), a loosening or decomposition.

immediately becomes coated with a bright rose-coloured deposit of copper. This, in fact, is the process used in electroplating. In the case of solutions of sodium chloride, also, the sodium liberated at one of the electrodes decomposes the water with production of hydrogen gas, which can be seen rising in bubbles from the electrode, and the solution acquires an alkaline reaction, as is shown by the fact that it turns reddened litmus blue. At the other electrode, chlorine is set free, and, dissolving in the water, yields a solution having bleaching properties, as is shown by the fact that it discharges the colour of a litmus solution. Whenever, therefore an electric current passes through a conducting solution, there is a movement of electrically charged matter through the liquid—charged particles of copper, or sodium, or chlorine, for example—and some of these particles move towards the one electrode, some towards the other electrode.

This conclusion was reached early last century by that great Natural Philosopher, MICHAEL FARADAY, who called the electrically charged moving particles which thus conveyed the electricity through the solution, by the happily chosen Greek term *ions* (*i.e.* wanderers); and this term is still retained.

That there is a relationship between the conducting power of solutions for electricity and their abnormal osmotic and cryoscopic behaviour was first clearly pointed out by the Swedish physicist Arrhenius in 1887.

SVANTE AUGUST ARRHENIUS was born at Wyk, in the neighbourhood of Upsala, Sweden, in 1859. After studying for five years at the University of Upsala, Arrhenius proceeded to Stockholm in 1881, where he carried out investigations more especially on the conduction of electricity by solutions, investigations which led him to conclude that the molecules of acids, when dissolved in water, undergo an extensive cleavage or dissociation into ions—the electrically charged particles which, according to Faraday, conduct the electric current through the solution. Since his views met with scornful rejection in Sweden, Arrhenius proceeded to Riga at the beginning of 1886 to continue his investigations in the laboratory of Wilhelm Ostwald, who soon after became Professor of Physical Chemistry in the University of Leipzig and the foremost teacher and expounder of this branch of science. Proceeding to the University of Würzburg in 1886, in order to study under the physicist Friedrich Kohlrausch, Arrhenius became acquainted with the work of van't Hoff and of Raoult on osmotic pressure and on the freezing-point of solutions, and was thus led to link up the abnormal osmotic

behaviour of acids, alkalis and salts with their dissociation into electrically charged ions. Thus arose the theory of electrolytic dissociation, the publication of which in 1887 marks the beginning of a new epoch in the development of our knowledge of electrically conducting solutions.

In 1891, Arrhenius was appointed lecturer and afterwards Professor of Physics at the Technical High School, Stockholm, where also his administrative ability gained for him, at a later time, the honour of being three times elected Rector. While in



SVANTE AUGUST ARRHENIUS.

Stockholm, Arrhenius devoted himself not only to the investigation of many problems arising out of or suggested by the new theories of solutions, but also to the discussion of problems in cosmic physics and to the investigation of the relations between toxins and anti-toxins. His valuable contributions to science received world-wide recognition, and the Nobel Prize in Physics was awarded to him in 1903. In 1905, Arrhenius, after declining an invitation to Berlin, was appointed Director of the Nobel Institute at Stockholm, a post which he held until he died in October 1927.



A man of generous proportions, physically as well as mentally, Arrhenius was a welcome guest at meetings of scientific societies both in Europe and in America, and he endeared himself to all who met him by his powers of conversation and his genial and kindly manner.

**Theory of Electrolytic Dissociation.**—It has been mentioned that even as early as 1884 Arrhenius had reached the conclusion that electrolytes in solution undergo a more or less extensive and spontaneous dissociation into positively and negatively charged ions. When, therefore, he found, from his study of the work of van't Hoff and of Raoult, that the substances which in solution give abnormally large osmotic pressures and abnormally great depressions of the freezing-point, are just those substances which, in solution, conduct the electric current (electrolytes), there flashed into his mind the idea that the products of dissociation which, as we have seen, may be assumed in order to explain the abnormally great osmotic pressure and depression of the freezing-points shown by salts in solution, are none other than the positively and negatively charged ions of the electrolytes. These ions lead an independent existence in the solution, have their specific properties and reactions, and behave, therefore, as independent substances.

The theory of electrolytic dissociation or ionisation enables one not only to explain the osmotic and cryoscopic behaviour of electrolytes in solution, but also to understand more clearly what is meant by an acid, an alkali and a salt.

**Definition of Acids, Alkalis and Salts.**—When a salt undergoes electrolytic dissociation, or ionises, the metal forms the positively charged ion, the *cation*; <sup>1</sup> and the acid part forms the negatively charged ion, the *anion*. Thus, for example, sodium chloride, NaCl, ionises into the positively charged cation, Na<sup>+</sup> (sodium ion), and the negatively charged anion, Cl<sup>-</sup> (chloride ion). In general, therefore, *a salt may be defined as a substance which, in solution, gives rise to positively charged and negatively charged ions*. In the case of acids, hydrogen ion forms the cation, so that hydrochloric acid gives the ions H<sup>+</sup> and Cl<sup>-</sup>, a dot and a dash being used in place of the plus and minus sign respectively. Nitric acid, similarly, gives the ions H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> (nitrate ion). The only property, in fact, which acids have in common is that of giving rise to hydrogen ion; and

<sup>1</sup> From the Greek *κατά* (kata), down, and *ίων* (ion), wandering. The cation is the ion which moves downstream, as it were, in the direction of flow of positive electricity. The anion, on the other hand, is the ion which, as it were, moves upstream (from *ana*=up), in the direction of flow of negative electricity.

it is to the presence of hydrogen ion that the so-called acid properties are to be ascribed. *An acid is a substance which in solution gives rise to hydrogen ion, and acid properties are the properties of hydrogen ion.* Dry tartaric acid or dry citric acid shows no acid properties. If brought into contact with dry litmus, the colour of the litmus is not affected; or if mixed with dry sodium bicarbonate, there is no evolution of carbon dioxide. If the tartaric acid or citric acid is dissolved in water, however, ionisation takes place with production of hydrogen ions, and the solution now gives a red colour to litmus and causes an evolution of carbon dioxide when added to sodium bicarbonate.

In the case of alkalis, *e.g.* sodium hydroxide ( $\text{NaOH}$ ), the anion is formed by the hydroxyl group, giving the ion,  $\text{OH}'$ , called hydroxide ion. That is to say,  $\text{NaOH}$  ionises with formation of  $\text{Na}'$  and  $\text{OH}'$ . Potassium hydroxide, calcium hydroxide and other alkalis also give rise to hydroxide ion, so that an alkali may be defined as a substance which in solution gives rise to hydroxide ion. *It is to the presence of hydroxide ion in solution that the general properties of alkalis are due.*

From the definitions which have been given, it will be clear that the term "salt," in its wider meaning, includes acids and alkalis; usually, however, it is applied only to those electrolytes which give rise neither to hydrogen ion nor to hydroxide ion.

In what has so far been said, mention has been made only of those electrolytes a molecule of which is capable of yielding two and not more than two ions. A molecule of sodium sulphate,  $\text{Na}_2\text{SO}_4$ , however, can give rise to three ions, namely, two sodium ions and one sulphate ion; and since the solution of sodium sulphate, as a whole, is neither positively nor negatively charged, the amount of electricity associated with one sulphate ion must be equal to that associated with two sodium ions. The amount of electricity associated with 1 gram-ion (ionic weight in grams) or 23 grams of sodium ion, is 96,540 coulombs; and as this is the smallest amount of electricity associated with the gram-ionic weight of any substance, it is regarded as the unit charge and called a *faraday*. Hence, the symbol of the sodium ion is written  $\text{Na}'$ , with only one plus sign or with one dot to represent one unit charge or one faraday, whereas the symbol of the sulphate ion is written with two negative signs or two dashes to represent two faradays. Thus,  $\text{SO}_4^{--}$  or  $\text{SO}_4''$ .

The theory of electrolytic dissociation is one of the most important and far-reaching theories in physical and chemical science. Not only does it afford an explanation of the electrical properties (conductivity, etc.) of electrolytic solutions, but it

co-ordinates a large number of apparently isolated and disconnected properties, such as osmotic pressure, depression of the freezing-point, elevation of the boiling-point, colour of salt solutions, and chemical and bio-chemical properties and reactions. When first published, the theory met with violent opposition—due to some extent to a misunderstanding of it—but now, although in a number of cases some extension, modification or re-interpretation of the theory is found to be necessary, the theory in its essentials is generally accepted as explaining the properties of electrolytic solutions.

**Degree of Ionisation.**—Although, according to the theory of Arrhenius, the molecules of electrolytes spontaneously undergo ionisation in solution, it does not necessarily happen that all the molecules thus break up. How, then, can one determine the degree of ionisation or the fraction of the salt molecules which, in any given case, undergoes ionisation? Various methods are available, but only one will be mentioned here.

The depression of the freezing-point, we have seen, depends on the total concentration of the solute particles, *i.e.* the concentration of un-ionised molecules *plus* ions. If, then, 1 gram-molecule of, say, sodium chloride is dissolved in 1 litre of water, and if the fraction  $\alpha$  of the salt undergoes ionisation, it is clear that there will be in solution  $(1-\alpha)$  gram-molecule of un-ionised molecules and  $2\alpha$  gram-molecules of ions, because each molecule on ionising gives two ions. The total amount of solute particles will therefore be  $(1-\alpha)+2\alpha$ , or  $(1+\alpha)$  gram-molecules. Owing to ionisation, therefore, there will be an increase in the number of solute particles from 1 gram-molecule to  $(1+\alpha)$  gram-molecules, and, consequently, the actual depression of the freezing-point ( $\Delta_{\text{actual}}$ ) will be greater than the theoretical depression ( $\Delta_{\text{theoretical}}$ ), or the depression which one would obtain if no ionisation took place, in the ratio  $(1+\alpha):1$ . Or,

$$\frac{\Delta_{\text{actual}}}{\Delta_{\text{theoretical}}} = \frac{1+\alpha}{1}.$$
 Thus, it was pointed out (p. 248) that a solution of sodium chloride containing 0.20 gram-molecule of salt in 1 litre of solution, freezes at  $-0.693^{\circ}\text{C.}$ , whereas the theoretical freezing-point is  $-0.372^{\circ}$ . Therefore,

$$\frac{0.693}{0.372} = 1.863 = 1+\alpha;$$
 or, the degree of ionisation,  $\alpha$ , is equal to 0.863. In this particular solution, 86.3 per cent. of the sodium chloride molecules undergo ionisation. The extent to which ionisation takes place, or becomes effective, increases with the dilution.

In the case of an electrolyte which can give rise only to two ions, the depression of the freezing-point cannot be more than

twice as great as that which would be given by an equimolecular solution of a non-electrolyte; and in the case of an electrolyte which can give rise to three ions (*e.g.*  $\text{Na}_2\text{SO}_4$ ), the depression cannot exceed three times the normal.

Although comparatively small differences are found in the degree of ionisation of different salts in moderately dilute solution, the extent to which acids and alkalis may undergo ionisation may vary enormously. Whereas, in the case, say, of hydrochloric acid, nitric acid, sodium hydroxide, etc., ionisation is almost complete in dilute solution, the degree of ionisation in other cases may be only a small fraction of 1 per cent. In solutions of equivalent concentration, therefore, the concentration of hydrogen ion or of hydroxide ion, and, consequently, the acid or alkaline properties of the solutions, may vary greatly. It is customary, therefore, to distinguish between *strong* electrolytes and *weak* electrolytes, *strong* acids and *weak* acids, *strong* alkalis and *weak* alkalis; strong electrolytes being such as undergo ionisation to a large extent, and weak electrolytes being such as undergo ionisation only to a slight extent.

## CHAPTER XVII

### ELECTRICITY AND CHEMISTRY

**Birth and Early Development of Electro-chemistry.**—In a previous chapter it was sought to point out and to emphasise that a chemical reaction must no longer be considered as involving merely a transformation of material but also a flow of energy; and it was also claimed that one of the chief characteristics of the scientific advance during the past hundred years has been the manner in which and the extent to which the different forms of energy have been transformed and utilised. In our study of the subject of combustion we had a glimpse into that branch of science, thermo-chemistry, which deals with the relations which exist between chemical energy and heat energy; and in the present chapter there will be discussed the relations which obtain between chemical energy and that other form of energy, the utilisation of which is so notable a feature of the past fifty years, electrical energy.

The birth of electro-chemistry, as this twin branch of science which deals with the relations between electricity and chemistry is called, may be dated from the time when, in 1791, LUIGI GALVANI (1737–1798), Professor of Anatomy in his native town of Bologna, observed the convulsive twitching of the muscle of a freshly dissected frog, each time the muscle and nerve were connected by two different metals.<sup>1</sup> It was a humble birth, surely, for a science which has revolutionised the world, which has made practicable the telegraph and the telephone, and has supplied mankind with many materials both of ornament and of use.

If it is to Galvani that we owe the observation in which electro-chemistry found its birth, it is to his fellow-countryman, ALESSANDRO VOLTA <sup>2</sup> (1745–1827), Professor of Natural Philo-

<sup>1</sup> The well-known pricking sensation and acid taste which are experienced when the tongue is touched by two different metals which are also in contact with each other, was first observed, about 1750, by a teacher of mathematics in Berlin, Johann Georg Sulzer.

<sup>2</sup> The intimate connection of Volta with electricity is held in remembrance by the use of the term *volt* as the unit of pressure (or *voltage*) of an electric current.

sophy in the University of Pavia, that the science owes its further development. Rightly interpreting the muscular contraction of the frog's leg as being due to the current of electricity which is produced whenever contact is made between two different metals separated from each other by a liquid conductor, Volta constructed an apparatus whereby a continuous current of electricity could be obtained through the transformation of chemical energy into electrical energy. When a strip of silver or of copper and a strip of zinc are partially immersed in a solution of sulphuric acid, Volta found that on connecting the free ends of the metals by means of a conducting wire, a current of electricity is obtained. By connecting a number of such cells together, so that the copper or silver plate of one was joined to the zinc plate of the next, Volta built up a battery—the famous *couronne de tasses*, or crown of cups—with which effects of the most notable character were obtained; and the *voltaic cell*, as it was called, was the scientific sensation and curiosity of the end of the eighteenth and the beginning of the nineteenth century. Cells of a similar but more efficient character were constructed by others, and the effect of the electric current was tried on a great variety of substances. In 1800, the first definitely and clearly recognised case of the decomposition of a chemical compound with the help of the electric current, was observed by Sir ANTHONY CARLISLE (1768–1840), Professor of Anatomy to the Royal Academy in London, and WILLIAM NICHOLSON<sup>1</sup> (1753–1815), who found that when an electric current is passed through water, hydrogen is evolved at one electrode and oxygen at the other.

It was, however, at the Royal Institution, London, that the chemical effects produced by the electric current were most fully investigated, with the result that, under the guiding genius of SIR HUMPHRY DAVY, the alkali metals, sodium and potassium, were isolated for the first time in 1807, by passing a current of electricity through molten caustic soda and molten caustic potash.

Such was the beginning of man's triumphant success in transforming chemical into electrical and electrical into chemical energy; and just as in the seventeenth century, science first began to burst into a wonderful blossom and “poets sang with emulous fervour the approach of the Golden Age,” so the invention of the voltaic cell, the isolation of the alkali metals and the rapid development of physical science, which took place

<sup>1</sup> Nicholson, who founded the scientific periodical, *Nicholson's Journal*, was, at different times, an official of the East India Company, a traveller for the firm of Wedgwood, a school teacher and a civil engineer.

in the early part of the nineteenth century, led to extravagant views as to what might be accomplished, even to realising, as Faraday conceived possible, "the once absurd notion of transmutation."

Important as were the results obtained by the use of the voltaic cells, when regarded from the purely scientific point of view, the cost of working the cells was very considerable, and it was not, therefore, until the introduction of the dynamo (made possible by the scientific researches of Faraday), that the



HUMPHRY DAVY.

industrial application of electricity became practicable. By means of the dynamo it has now become possible to obtain a cheap supply of electrical energy, and the *couronne de tasses* of Volta has been replaced by multitudes of humming dynamos; and in place of the few globules of metallic sodium which Sir Humphry Davy succeeded, with much difficulty, in isolating, that and many other substances are now produced by hundreds and thousands of tons in the electro-chemical factories of the world.

HUMPHRY DAVY, who first gave to electro-chemistry a solid

experimental foundation, was born at Penzance in Cornwall on December 17th, 1778. Owing to the death of his father and the necessity of earning a living, Davy, at the age of 16, became apprenticed to a surgeon-apothecary in his native town. In 1798, however, having become greatly interested in the study of chemistry through reading a translation of Lavoisier's *Éléments de Chimie*, Davy accepted the post of Superintendent of the *Pneumatic Institution*—"an hospital for patients, a laboratory for experimental research and a theatre for lecturing"—which had just been founded at Clifton, near Bristol, by a Dr. Thomas Beddoes, for the study of the physiological properties of gases. Here, Davy laid the foundation of his reputation by his discovery of the intoxicating and anæsthetic properties of nitrous oxide (or "laughing gas"), a gas discovered in, or before, 1772 by Priestley. Some years later, in 1801, recognised as a man of exceptional gifts and scientific ability, Davy was appointed lecture-assistant and, later, Professor of Chemistry at the Royal Institution, London, an institution founded in 1799, and intended to interest the aristocracy and fashionable society of London in science.<sup>1</sup>

While at the Royal Institution, Davy carried out investigations in electro-chemistry, which established his reputation as one of the most brilliant chemists of his time; and he demonstrated, also, that chlorine—discovered by Scheele in 1774 and called by Lavoisier oxy-muriatic acid—is an element and not a compound.

In 1813, Davy resigned his professorship at the Royal Institution, and, accompanied by Lady Davy and by his assistant, Michael Faraday, spent two years travelling in Europe. He took with him, however, a "commodious, portable apparatus" with which, during his stay in Paris and elsewhere, he carried out chemical investigations, including an investigation of the properties of the recently discovered element iodine. Returning to England in 1815, Davy investigated explosions of fire-damp in coal mines, and was thereby led to the invention of the miner's safety lamp (p. 170). During the remaining years of his life, he devoted himself mainly to work of public utility.

A brilliant conversationalist, Davy had a keen intellect and

<sup>1</sup> The Royal Institution was founded by Count Rumford, who, before being created a Count of the Holy Roman Empire by the Elector Palatine of Bavaria, bore the name of Benjamin Thompson. Born in the State of Massachusetts in 1753, Thompson's royalist views led him to retire from the regiment of militia which he had entered and to come to England in 1776, where he became a Civil servant and engaged in scientific pursuits. At a later date he married the widow of Lavoisier. He died in 1814.



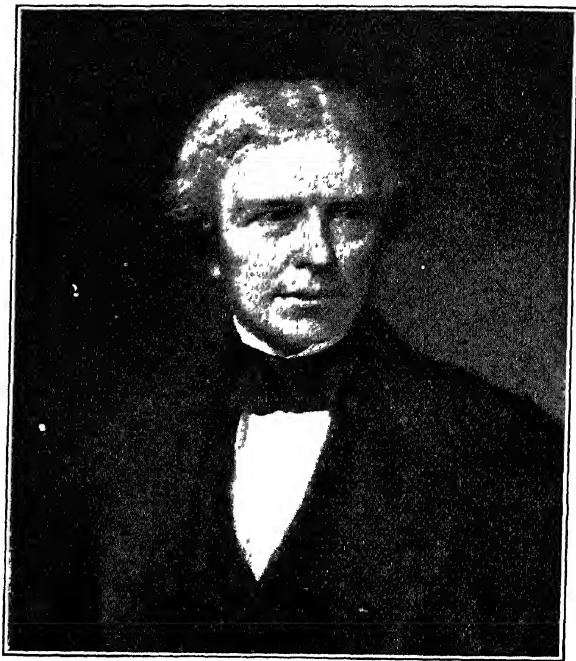
a sensitive and poetic temperament. He was a facile and pleasing versifier, although doubtless the opinion of the poet Coleridge that "if Davy had not been the first Chemist, he would have been the first Poet of his age," was biassed by an over-enthusiastic affection. He was also an exceptionally expert experimentalist and an attractive lecturer, and the fashionable society of London attended his discourses in large numbers. Raised by his genius and good fortune, with almost meteoric swiftness, from comparatively poor surroundings to a position among the most famous scientific discoverers of the day and introduced into a fashionable society which lionised him, it is perhaps not altogether to be wondered at that the quondam surgeon-apothecary's apprentice developed a somewhat haughty and superior manner, and posed as the "grand seigneur" and man of the world.

In 1812, Davy received the honour of knighthood and in 1818 he was created a baronet—an exceptionally high honour at that time for a man of science; and for seven years, 1820–1827, he was elected President of the Royal Society, of which he had been elected a Fellow in 1803. In 1826 his health began seriously to decline, and on May 29th, 1829, he died at Geneva, where, in the Protestant cemetery of Plainpalais, he was buried.

If it was Sir Humphry Davy who laid the experimental foundation of electro-chemistry, it is to his more famous assistant and successor at the Royal Institution, Michael Faraday, that we owe the discovery of the laws of electrolysis and of magneto-electric induction which have made possible the modern development of electro-chemical industry.

MICHAEL FARADAY was born at Newington Butts (now incorporated in the south-eastern district of London), on September 22nd, 1791. Son of a blacksmith and reared in an atmosphere of penury, Faraday, at the age of thirteen, became errand boy to a bookseller and bookbinder in London, and a year later, bookbinder's apprentice. Even at this early age his mind was alert, eager, original, enquiring; and although his schooling had taught him merely the rudiments of reading, writing and arithmetic, he devoured with avidity the books which in the course of his work as a bookbinder, passed through his hands. And so it came about that the chance reading of Mrs. Marcet's *Conversations on Chemistry* and of an article on electricity in the *Encyclopædia Britannica*, turned the thoughts of the young bookbinder to science and shaped the future course of his life. "Do not suppose," he wrote in after life, "that I was a very deep thinker,

or was marked as a precocious person. I was a very lively, imaginative person, and could believe in the *Arabian Nights* as easily as in the *Encyclopædia*. But facts were important to me, and saved me." In these concluding words we have expressed the guiding principle of Faraday's life. He had an intense dislike of "doubtful knowledge," and would not rest content until hypotheses and speculations had been put to the actual test of experiment.



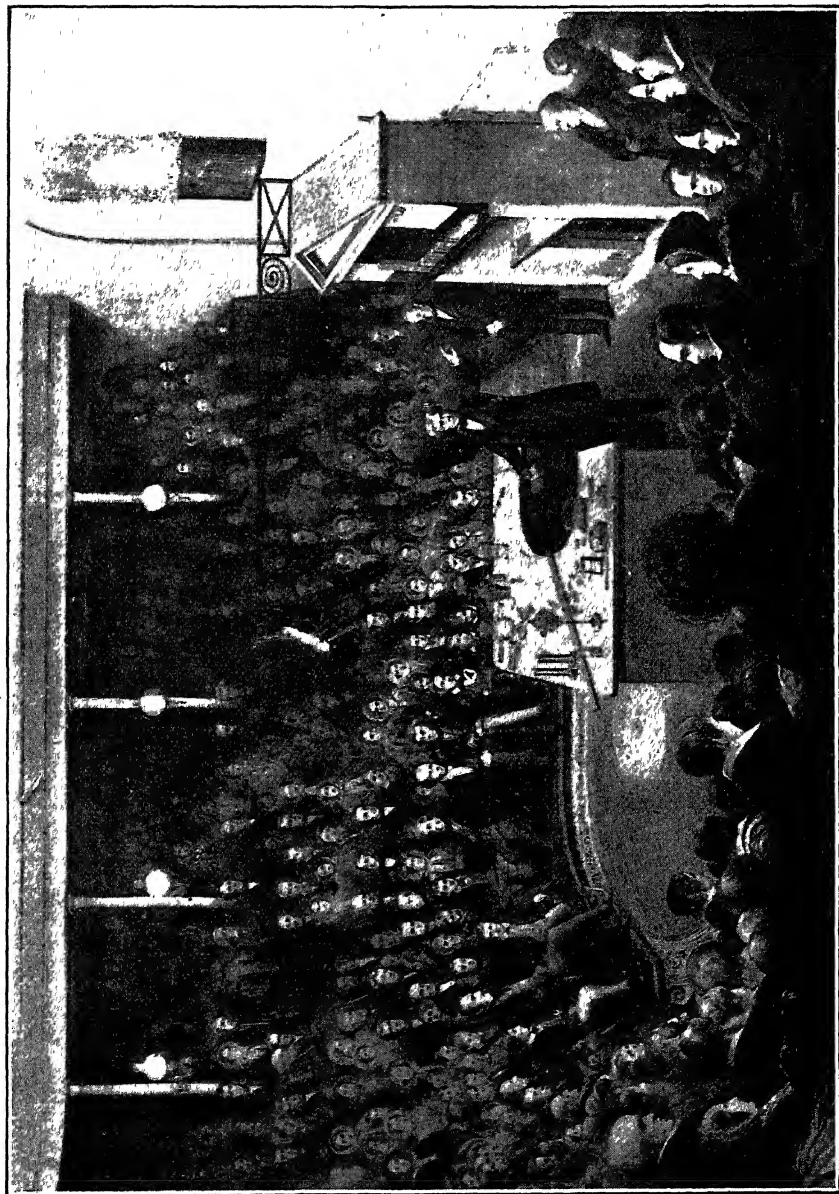
MICHAEL FARADAY.

Reproduced from the portrait by Blaikley by permission of the Royal Society.

Finding the lure of science irresistible, Faraday wrote to Sir Humphry Davy, some of whose lectures he had attended, and expressed his desire to enter into the service of science; and in 1813, Davy made him his laboratory assistant at the Royal Institution. There, Faraday received his first systematic training and there, also, he passed the whole of his scientific life, occupying successively the posts of Superintendent of the house and laboratory (1821), Director of the Laboratory (1825), and Professor of Chemistry (1827). Through his work at the Royal Institution, Faraday came to be acknowledged as the

foremost investigator in physical science of his time and one of the most attractive lecturers.

Faraday's first important scientific work was the liquefaction,



FARADAY LECTURING BEFORE THE PRINCE CONSORT AT THE ROYAL INSTITUTION, DECEMBER 27, 1855.

in 1823, of chlorine and of other gases which hitherto had been regarded as non-liquefiable (p. 120); and in 1825, he discovered the substance benzene, which is now so extensively employed both as a constituent of motor fuel and in chemical manufacture. Important, however, as were the purely chemical investigations carried out by Faraday, it is on his investigations and discoveries in the domain of physical-chemistry and of physics that his fame mainly rests—on his researches on voltaic and frictional electricity, on the magnetic rotation of the plane of polarised light, on the electrolytic decomposition of solutions, and, more especially, on his discovery of electric induction and magneto-electric induction.

In 1824, Faraday was elected a Fellow of the Royal Society, and, in later years, the honours of the world-wide realm of science and learning, the honours of Universities and learned Societies, were heaped upon him in greater measure than on any other scientific worker. In spite of this, however, Faraday retained the simplicity of character, the deep religious feeling and the comparative indifference to rank, wealth and the attractions of society, which had marked his early life. The impelling force in the life of Faraday was the desire to know, not merely to acquire an understanding of what was already known, but to extend the boundaries of knowledge; and when, on August 25th, 1867, his life came quietly to an end in the house on Hampton Court Green granted to him by Queen Victoria, it could be said of him: "His was the glory of holding aloft among the nations the scientific name of England for a period of forty years."

**Mechanism of Electrolysis.**—During a great part of last century there was much discussion as to the way in which the electric current was conveyed through a solution, and it was only in 1886 that a satisfactory explanation of the constitution of electrolytic solutions and of the mechanism of electrolysis was given by the Swedish physicist, Svante Arrhenius. Instead of assuming, as Faraday did, that the molecules of an electrolyte are broken up by the electric current—a view which has since been shown to be incorrect—Arrhenius assumed that the molecules of an electrolyte when dissolved in water, *dissociate or ionise of their own accord*, and the part-molecules which are formed are the electrically charged ions. In the light of this hypothesis, the fact that addition of sodium chloride, or of any other salt, acid or alkali to water, yields a solution which conducts the electric current, becomes readily intelligible. These solutions, according to the hypothesis, contain free, positively charged *cations*, and free, negatively charged *anions*. When,

therefore, two electrodes are placed in the solution of an electrolyte and connected with an electric battery, the positively charged electrode (the *anode*) attracts the negatively charged ions, the *anions*; and the negatively charged electrode (the *cathode*) attracts the positively charged ions, the *cations*. These anions and cations move in opposite directions through the solution, and give up their charges at the electrodes; they transport or convey the electricity through the solution, and it is this movement or procession of electrically charged particles that constitutes what is called the electric current in the solution.

This explanation of the passage of a current through a solution is not a mere speculation, not a mere phantasy, for it is easy to demonstrate not only that there is a movement of the ions through the solution, but also that the ions move with different velocities. There is a pretty experiment, devised by A. A. NOYES and A. A. BLANCHARD, by which one can make this clear. Into the bend of a U-shaped tube (Fig. 54) is placed a solution of potassium chloride to which sufficient gelatin has been added to make the liquid set to a jelly; and the solution is coloured red by the addition of a substance called phenolphthalein and a little alkali. (Phenolphthalein is a colourless substance which yields a deep-red colour with alkalis, or solutions containing hydroxide ions; and the red colour is again destroyed by addition of acids, or solutions containing hydrogen ions.) After the solution in the bend of the tube has set, a further quantity of the same coloured solution is poured into one limb of the tube (D), while into the other limb (E) is poured the same solution after it has been decolorised by the addition of the requisite amount of acid.

Above this colourless layer of gelatin is placed a quantity of a mixed solution of caustic potash (potassium hydroxide) and potassium chloride (G), while in the other limb of the tube is

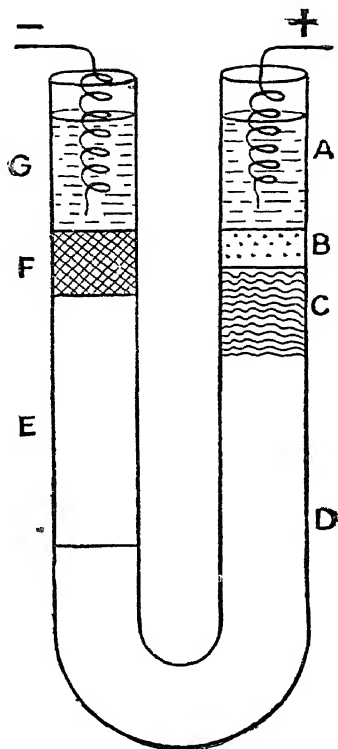


FIG. 54.—Migration of ions.

placed a mixed solution of hydrochloric acid and copper chloride (A). An electric current is now passed through the solutions in the tube, by placing a wire, connected with the positive pole of the battery, in the solution of hydrochloric acid and copper chloride, and a wire, connected with the negative pole of the battery, in the solution of caustic potash and potassium chloride. After the current has passed for some time it is found that the hydrogen ions (from the hydrochloric acid), moving from the positive towards the negative electrode, have decolorised the reddened phenolphthalein, and have produced, therefore, a colourless band (C) of a certain depth. The blue-coloured copper ions (from the copper chloride), which move in the same direction as the hydrogen ions but with a slower speed, follow on into the colourless band produced by the hydrogen ions, and give a blue colour to the gelatin (B). In the other limb of the tube, the hydroxide ions (from the caustic potash), moving from the negative to the positive electrode, pass into the colourless gelatin and produce with the phenolphthalein there a band of red (F). This band is deeper than the band produced by the copper ions, but not so deep as that produced by the hydrogen ions, from which it may be concluded that the hydrogen ions move faster than the hydroxide ions, and the latter faster than the copper ions.

It should be borne in mind, however, that it is not only when in a state of solution that an electrolyte conducts the electric current; it conducts also when fused, or converted into the liquid state by heat. One may conclude, therefore, that an electrolyte, when fused, dissociates into ions, and that the mechanism of electrolysis is essentially the same in the case of a fused electrolyte as in the case of an electrolyte in solution. On this fact depends, as will be learned more fully later, the industrial production of such metals as sodium and aluminium.

When the electric current is passed through a solution, the positively charged cations—hydrogen ion of acids and metal ions of salts—are discharged at the cathode, while the negatively charged anions—hydroxide ion of alkalis and acid radicles of salts—are discharged at the anode. In many cases, the primary products of electrolysis which are formed when the ions lose their electric charge, may give rise to secondary products, through decomposition or through interaction with the electrodes or with the solution. Thus, when a solution of sodium sulphate is electrolysed, the sodium atoms liberated at the cathode react with the water to form hydrogen and a solution of sodium hydroxide:  $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$ . Similarly, when the

sulphate ion,  $\text{SO}_4^{--}$ , is discharged at the anode, reaction with water gives rise to sulphuric acid and oxygen:  $2\text{SO}_4 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{O}_2$ . The hydrogen and oxygen, therefore, which are produced by the electrolysis of a dilute aqueous solution of a salt, are not primary but secondary products of electrolysis.

**Laws of Electrolysis.**—The theory of ionisation in solution enables one not only to understand the mechanism of electrolysis, but also the laws of electrolysis, which were discovered experimentally by Faraday and are generally known as Faraday's laws. FARADAY'S FIRST LAW states: *When an electrolyte is decomposed by the electric current, the amount of decomposition is proportional to the quantity of electricity which flows through the solution.* This law follows at once from the theory of Arrhenius, according to which each ion carries a certain charge or amount of electricity. A given weight of the ion is, therefore, associated with a definite amount of electricity. Double the weight of that ion will therefore be associated with double the amount of electricity, and, consequently, the amount of electricity which is conveyed by the ions through the solution will be proportional to the weight of the ions discharged at the electrode; or, the amount of electricity will be proportional to the amount of electrolyte decomposed. It is on the basis of this law that *voltameters* or *coulommeters*, i.e. instruments for measuring the amount of electricity or the number of units, *coulombs*, of electricity which pass through a circuit, are constructed.

FARADAY'S SECOND LAW states: *When the same current (or the same amount of electricity) is passed through solutions of different electrolytes, the weights of ions discharged are in the ratio of their chemical equivalents; the equivalent being given by the ionic weight divided by the valency of the ion.* Thus, if the same amount of electricity is passed through solutions of sulphuric acid, silver nitrate and copper sulphate, the weights of hydrogen, silver and copper respectively which are liberated at the cathodes of the electrolytic cells, will be in the ratio

1 : 108 :  $\frac{63.6}{2}$ . (The atomic or ionic weights of hydrogen, silver and copper are here taken as 1, 108 and 63.6 respectively.) One can therefore say: One gram-equivalent of any ion is associated with a definite amount of electricity—the amount being, as we have seen, 1 faraday or 96,540 coulombs; and in order that 1 gram-equivalent of an ion (any ion) may be discharged at an electrode, this unit amount of electricity, 1 faraday, must be passed through the solution. In writing the symbols of the ions, each positive or negative sign (or each dot and dash)

represents 1 faraday or 96,540 coulombs of electricity. One can, therefore, at once calculate the weight of an ion which will be deposited by a given amount of electricity, the weight deposited by 1 coulomb being known as the *electro-chemical equivalent* of the ion.

**Voltaic Cells.**—Not only does the theory of Arrhenius afford an explanation of the process of electrolysis whereby electrical energy is transformed into chemical energy, or the potential energy of chemically reactive substances, but it helps us also to understand the reverse process of the transformation of chemical energy into electrical energy, as it occurs in the different voltaic cells.

One of the simplest of the voltaic cells is that known as the Daniell cell,<sup>1</sup> which consists of an electrode of copper immersed

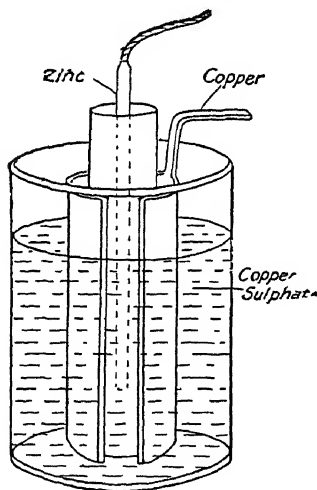
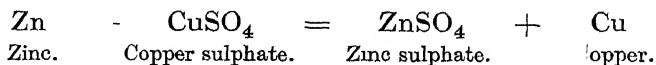


FIG. 55.—Daniell cell.

in a solution of copper sulphate, and an electrode of zinc immersed in a solution of zinc sulphate. The latter solution is contained in a porous pot which prevents the mixing of the two solutions (Fig. 55). When the copper electrode and the zinc electrode are connected by means of a conductor, an electric current flows through this conductor from the copper to the zinc. Moreover, if an electric motor, for example, is inserted in the circuit, it will be caused to rotate, and so mechanical work can be done. What, then, is the source of this supply of energy which, either in the form of electrical energy, or in the form of the mechanical energy into which it is

transformed, is given out by the Daniell cell?

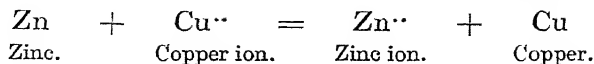
When a strip of zinc is immersed in a solution of copper sulphate, copper is deposited on the zinc, and at the same time an equivalent amount of zinc passes into solution. The chemical process which takes place may therefore be represented by the equation :



<sup>1</sup> Invented, in 1836, by John Frederic Daniell (1790–1845), Professor of Chemistry at King's College, London.



Or, since, according to the theory of Arrhenius, the copper sulphate and the zinc sulphate are ionised in solution, and since the sulphate ions remain unchanged in solution, the essential nature of the process will be represented by the equation :



This is a reaction which takes place spontaneously ; that is, zinc and copper sulphate represent a system with a certain amount of potential energy, and it is capable, therefore, of doing work or of yielding energy. How, then, can one secure the transformation of the chemical energy into electrical energy ? The answer is : By so arranging matters that the change represented by the above equation takes place by means of the electrically charged particles, the ions, which are formed when a salt is dissolved in water.

When a copper plate is immersed in a solution of copper sulphate, it becomes positively charged relatively to the solution, because (so it is assumed) copper ions (in unweighable amount) take up electrons from the metal and become neutral atoms of copper. On the other hand, when zinc is immersed in a solution of zinc sulphate, the metal readily gives up electrons and passes into solution (also in unweighable amount) as positively charged zinc ions. The zinc electrode, therefore, becomes negatively charged relatively to the solution. Consequently, when the two electrodes are connected by means of a metallic conductor, there is a flow of negative electrons through the conductor<sup>1</sup> from the electrode with excess of electrons (the zinc electrode), to the positively charged electrode or electrode with a defect of electrons (the copper electrode). In other words, a current of negative electricity flows through the conductor from the zinc to the copper electrode. As the electrons arrive at the copper electrode, they are taken up by the copper ions in the solution, and the neutral copper atoms which are thereby formed are deposited as metallic copper on the electrode. On the other hand, in proportion as the electrons flow away from the zinc electrode, zinc passes into solution as zinc ions ; and so the flow of electricity continues. In the voltaic cell, therefore, just as when zinc is immersed in a solution of copper sulphate, so copper passes out of solution to form metallic copper, and at the same time an equivalent amount of zinc passes into solution. Instead, however, of the reaction between zinc and copper sulphate taking place at one point by direct contact, whereby the chemical energy is converted into heat, the reaction in the Daniell cell takes place

<sup>1</sup> In metallic conductors, electricity is carried only by electrons.

in two parts, at the two electrodes, and the chemical energy now appears in the form of electrical energy.

Although in a metallic conductor the electricity is carried only in one direction by the negatively charged electrons, in solutions the electricity is carried by both the cations and the anions. In the Daniell cell, for instance, the copper ions move towards the copper electrode, whereas the sulphate ions move towards the zinc electrode in order to balance the positive electricity carried into the solution by the zinc ions.

Although of interest from the theoretical point of view, the Daniell cell is less convenient than others, and is not now in general use.

A better-known cell, widely employed for working telephones and electric bells, is the Leclanché cell<sup>1</sup> (Fig. 56). This very

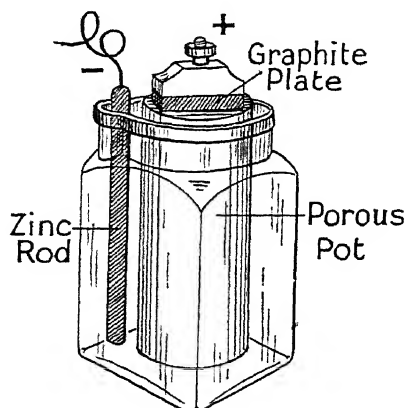


FIG. 56.—Leclanché cell.

simple cell consists of a vessel containing a solution of sal-ammoniac (ammonium chloride), in which is immersed a zinc rod which acts as the negative pole of the cell. Standing in the vessel of sal-ammoniac is a porous pot in which there is a graphite plate packed round with granules of graphite and black oxide of manganese (manganese dioxide). The porous pot also contains a solution of sal-ammoniac, and the graphite plate acts as the positive pole of the cell. When the cell is in

use, zinc passes into solution, while the hydrogen which is produced at the graphite plate is oxidised to water by the oxide of manganese, and so is prevented from forming a non-conducting layer on the electrode, and thereby stopping the current.<sup>2</sup> The electrode is thereby "depolarised" as it is said. When the cell becomes exhausted, its activity can be renewed by replacing the spent liquid by a fresh solution of sal-ammoniac.

The Leclanché type of cell has, in recent years, passed into

<sup>1</sup> Invented by the French physicist Georges Leclanché in 1868.

<sup>2</sup> The ammonium chloride in solution gives rise to ammonium ions (consisting of the positively charged group of atoms  $\text{NH}_4$ ), and to chloride ions or negatively charged chlorine atoms. When the cell is in action, the zinc passes into solution as zinc ions; and the ammonium ions move to the graphite pole and there lose their positive charge by combining with electrons. The discharged ammonium ions then react with the water to form ammonium hydroxide and hydrogen.

world-wide use owing to its modification to form the common dry cell of to-day. In this "cell" there is a zinc container which also acts as the negative pole of the cell, and inside this is placed the graphite plate or rod with its depolariser packing, the latter being separated from the zinc container by a layer of paper which, as well as the whole contents of the cell, is soaked with a solution of sal-ammoniac (Fig. 57). Sometimes the graphite rod and depolariser are separated from the zinc container by a paste made from flour and a solution of sal-ammoniac. Hundreds of millions of such dry cells are now in use for flashlight lamps, bells, telephones, radio-batteries, etc.

Just as the *energy* of falling water depends not only on the amount of water but also on the height through which it falls, so the electrical energy given out by a voltaic cell depends not only on the amount of electricity (measured in coulombs) but

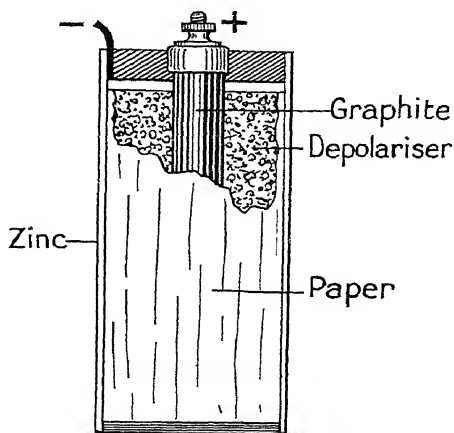


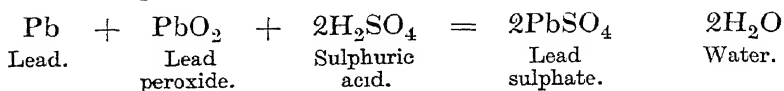
FIG. 57.—Dry cell.

also on the *electromotive force* (e.m.f.) of the cell, or what is sometimes called the voltage or electrical pressure; the energy being equal to the product of the e.m.f. and the amount of electricity, *i.e.* volts  $\times$  coulombs. The electrical energy of 1 volt-coulomb is equivalent to 0.24 calorie. The e.m.f. of the Daniell cell is 1.07 volt, and that of the Leclanché cell, about 1.5 volt.

Although, as has been said, the much more efficient dynamo has superseded the voltaic cell as a source of electricity for industrial purposes, there is one cell which occupies an important place as an auxiliary to the dynamo. This is the lead accumulator, or storage cell. This cell consists of plates of lead and of lead peroxide ( $\text{PbO}_2$ ), immersed in a solution of sulphuric acid, of specific gravity about 1.2. On joining these two sets of plates by means of a conductor, a current of electricity flows through the conductor from the lead peroxide plates to the lead plates.<sup>1</sup>

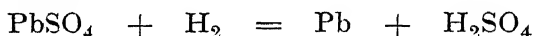
<sup>1</sup> Confusion is apt to arise here. The direction of flow of electricity can be detected only by its effect, say, on a magnet, and, traditionally, the direction of a current has been defined as the direction in which positive electricity would have to flow in order to deflect a magnet in a particular way. In the case of a metallic conductor, however, it is now known that the electricity is carried only by

The chemical reaction, the energy of which is transformed into electrical energy, is the conversion of the lead and lead peroxide into lead sulphate, as shown by the equation :

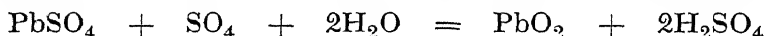


When this reaction has taken place, no more electricity is given out; the cell is "run down" or "discharged." Since the process of discharge is, as the equation shows, accompanied by the production of water, the sulphuric acid in the cell becomes more dilute, or its specific gravity falls; and, therefore, one can follow the process of discharge by determining the specific gravity of the acid by means of a hydrometer.

The lead accumulator has the great advantage over the other voltaic cells mentioned, in that the discharged cell can readily be re-charged, by sending a current of electricity—obtained, say, from a dynamo—through the cell in the opposite direction to that of the current which the cell itself gives. In this process, the sulphuric acid is electrolysed and the hydrogen ions, discharged at one electrode, convert the lead sulphate into lead and sulphuric acid :



At the other electrode, the sulphate ions react with the lead sulphate and water to form lead peroxide and sulphuric acid :



The electrodes are thereby transformed to their original state, with regeneration of sulphuric acid. During the process of charge, therefore, the specific gravity of the acid rises. The fully charged cell has an e.m.f. of about 2.2 volts.

When all the lead sulphate has been destroyed and the cell is fully charged, continued passage of the electric current brings about an electrolysis of the water with evolution of hydrogen and oxygen. "Gassing," as it is called, is therefore a sign that the cell is fully charged.

In the manner just described, the electrical energy from the dynamo is converted into potential, chemical energy; and in this form the energy is stored and is available for use just when and where it is required. This lead storage cell is one which

negatively-charged electrons which, of course, travel in the opposite direction to that assumed for the flow of positive electricity. In the above case, positive electricity does not flow through the conductor from lead peroxide to lead, but rather, negative electricity flows from the lead plate to the lead peroxide.

has a multitude of uses, such as giving current for electric lighting on a large scale (as an auxiliary to the dynamo), or for the lighting of motor cars; for energising the self-starter of motor cars or for driving cars and motor boats; and for many other purposes where a readily transported supply of energy is desired.

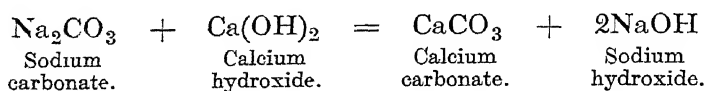
**Electro-chemical Industries.**—The application of electricity to chemical manufactures has produced an industrial revolution. Not only have electro-chemical processes more or less completely displaced the older chemical methods employed for the manufacture of such substances as caustic soda and of chlorine, or for the isolation of such metals as sodium, potassium, calcium, magnesium, and aluminium, but they have made possible also the discovery and economic production of many new substances of great value.

One of the earliest industrial uses to which electricity was put was to the coating of cheaper with more expensive, or less resistant with more resistant metals, by a process known as *electro-plating*, a process which has been largely used from before the middle of last century. At the present day the process is applied not only to the plating of the cheaper metals with silver and gold, for the production, for example, of relatively inexpensive table-ware and jewellery, but the electro-plating of lead alloys with copper (for ornamental purposes), and of iron or steel with brass, nickel, chromium and other metals, is very extensively carried out. Nickel, a metal much used on account of its white colour and its power of resisting atmospheric conditions without tarnishing, is more extensively applied in plating than any other metal, but the still harder and more resistant metal chromium is now displacing nickel for the plating of motor-car fittings—lamps, radiators, etc.—sanitary fittings, scientific apparatus, etc.

In theory, the process of electroplating is comparatively simple, and consists in passing a current of electricity through a solution of a salt of the metal with which the article is to be plated, the article to be plated being made the cathode, while the anode consists of a plate of the metal which is to be deposited. The process, in fact, is one of electrolysis (p. 264). Simple, however, as the process may be in theory, knowledge and care are necessary if uniform plating of good quality is to be achieved, for the nature of the deposit, its colour, lustre, cohesion and other qualities are affected by the composition and concentration of the solution, as well as by its temperature, acidity, etc., and by the *current density* used. By current density is meant the strength of

current (amperes) per unit of area of the object to be plated. Increase of current density leads to the production of a spongy and inferior deposit.

Formerly, for the production of **sodium hydroxide** or caustic soda, a solution of sodium carbonate was boiled with slaked lime (calcium hydroxide). Double decomposition, as it is called, takes place with formation of calcium carbonate, which separates out in the solid state, and sodium hydroxide which remains in solution. The reaction is represented by the equation :



Nowadays, however, this purely chemical process is being superseded to a considerable extent by an electrolytic process in which not only caustic soda but also chlorine and hydrogen are produced. When a solution of sodium chloride or common salt is electrolysed, chlorine is evolved at the anode while the sodium ions, discharged at the cathode, react with the water and yield hydrogen and a solution of sodium hydroxide. Many different types of electrolytic cell have been invented for the industrial production of caustic soda and chlorine. When a pure caustic soda is desired, a large covered-in tank is employed, filled with a solution of sodium chloride in which are immersed graphite electrodes which serve as anodes. At these electrodes chlorine is evolved, and passes away through a pipe in the roof of the tank. Along the floor of the cell mercury is allowed to flow in a slowly moving stream. This forms the cathode, and the sodium, which is liberated at the cathode, dissolves in the mercury. This solution of sodium in mercury flows out at the end of the tank and is treated with water. The sodium reacts with the water to form a solution of caustic soda and hydrogen, and the mercury is then passed through the cell again.

When chlorine is the chief product of the electrolysis, the Nelson cell<sup>1</sup> (Fig. 58) is very extensively employed in America and elsewhere. In this cell, a perforated steel cathode is separated from the brine solution by a porous diaphragm of asbestos, and graphite anodes are immersed in the brine. When the current is passed, chlorine is evolved at the anode and passes through a pipe in the slate roof of the cell, while sodium is liberated at the steel cathode. This sodium reacts with steam which is blown into the space around the cathode, and the hydrogen which is formed is collected and forms a valuable

<sup>1</sup> Invented by H. R. Nelson in 1914.

by-product, while the solution of caustic soda drips down into a well from which it can be run off. This solution contains a considerable quantity also of sodium chloride, most of which, however, crystallises out, when the caustic soda is concentrated. In America, especially, large quantities of soda-lye (solution of caustic soda) are transported in tank waggons for use in the manufacture of soap, etc.

Solid caustic soda is obtained from the solutions by evaporating off the water, but in order to free it entirely from water, the caustic soda must be heated to a temperature above its melting-point. The molten caustic soda is then run into iron drums or into moulds in which it solidifies in the form of sticks. It forms a white crystalline, very hygroscopic solid, which undergoes deliquescence when exposed to the air.

Caustic soda is very soluble in water, and the solution has the soapy feeling characteristic of alkalis.

By electrolysis a solution of potassium chloride (KCl), the compound, *potassium hydroxide* (KOH), which is very similar in its properties to sodium hydroxide, is obtained.

For the **chlorine** which is produced in the electrolytic process, there has developed an ever-widening range of application. Under ordinary conditions, chlorine is a greenish-yellow coloured gas<sup>1</sup> with a characteristic odour. It was first obtained by SCHEELÉ by heating hydrochloric acid with manganese dioxide, and was first shown to be an element by DAVY. When inhaled, even in small quantities, chlorine exerts an irritating and destructive action on the tissues of nose, throat and lungs, and it was the first poison gas to be used in the Great War. It is liquefied at the ordinary temperature by a pressure of about 6 atmospheres, and large quantities of liquid chlorine are now put on the market and transported in steel cylinders.

The most important use to which chlorine is put is for bleaching various materials, such as wood-pulp, cotton, etc.,

<sup>1</sup> Hence the name of the element, from the Greek *χλωρός* (chlōros), greenish-yellow.

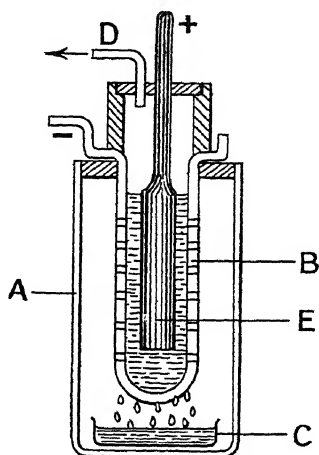
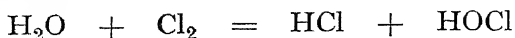


FIG. 58.—Nelson cell.

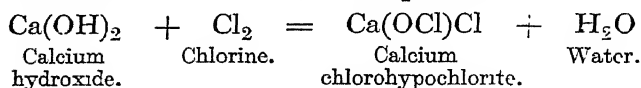
A, steel tank; B, asbestos diaphragm surrounded by a perforated steel cathode; C, trough in which the solution of caustic soda collects; D, tube through which the chlorine escapes; E, graphite anode.

for the manufacture of paper and textiles. This bleaching action depends on the fact that chlorine reacts with water to form hydrochloric acid (HCl) and another acid known as *hypochlorous acid* (HOCl), thus :



The hypochlorous acid so formed, acts as a powerful *oxidising agent* because of the readiness with which it gives up oxygen. Oxidisable organic dyes, therefore, are oxidised by hypochlorous acid to colourless compounds ; that is, they are bleached.

For convenience of transport, much of the chlorine which is produced is passed over slaked lime, which reacts with the chlorine and gives rise to *bleaching powder*, or chloride of lime, as it is popularly called. The essential constituent of bleaching powder (which also contains excess of slaked lime) is a compound known as calcium chlorohypochlorite, the above reaction taking place in accordance with the equation .



When calcium chlorohypochlorite is dissolved in water, it yields the ions  $\text{Ca}''$ ,  $\text{Cl}'$  and  $\text{OCl}'$  ; and when an acid, *e.g.* sulphuric acid ( $\text{H}_2\text{SO}_4$ ), is added, hydrogen ions unite with the hypochlorite ions ( $\text{OCl}'$ ) to form hypochlorous acid, which then exercises its oxidising (bleaching) action.

If the electrolysis of sodium chloride is carried out in a simple, undivided cell, so that the chlorine formed at the anode has ready access to the sodium hydroxide formed at the cathode, the salt, *sodium hypochlorite* ( $\text{NaOCl}$ ), is formed in the solution. The solution of this salt, which is akin to bleaching powder, has a powerful bleaching and antiseptic action.

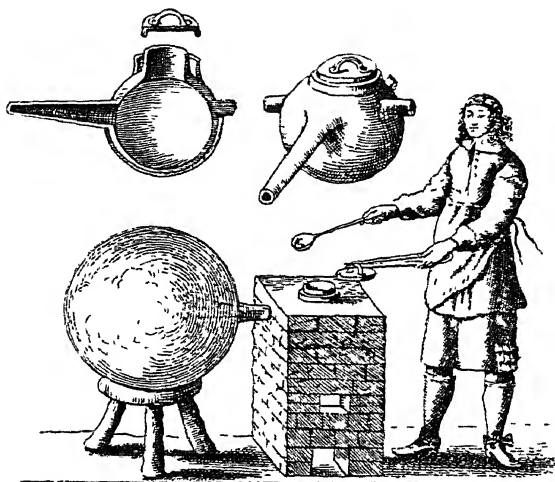
By electrolysing a *hot* solution of potassium chloride there is formed the white crystalline salt, *potassium chlorate* ( $\text{KClO}_3$ ), a salt first isolated by BERTHOLLET about 1786 and used, not only in the manufacture of fireworks and explosives but also, to some extent, medicinally. It is also used, as has been pointed out, for the preparation of oxygen in small amounts.

Although it is mainly for use as a bleaching agent that chlorine is manufactured, it is now also very widely employed for the sterilisation of water and as a disinfectant. It finds also very widespread application for the de-tinning of tinned cans and in the manufacture of many chemical compounds, *e.g.* carbon tetrachloride, phosgene, etc.

The hydrogen which is also produced during the electrolysis

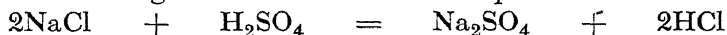


of sodium chloride, can be burnt in chlorine, and so give rise, by direct combination, to hydrogen chloride (HCl). This compound, a colourless gas at the ordinary temperature, dissolves very readily in water, 1 volume of water dissolving about 500 volumes of the gas. The solution of hydrogen chloride in water forms the important acid known as *hydrochloric acid* (muriatic acid<sup>1</sup> or spirit of salt). The hydrochloric acid produced synthetically by the direct combination of hydrogen and chlorine is very pure, and has displaced to a considerable extent the acid produced by the older chemical method—used doubtless by



Glauber's furnace for distillation and sublimation.

JOHANN RUDOLF GLAUBER (1604–1668) in the seventeenth century—of heating sodium chloride with sulphuric acid :



Sodium chloride.      Sulphuric acid.      Sodium sulphate.      Hydrogen chloride.

**The Halogens.**—*Chlorine* is the most important member of a family of four elements which are chemically closely related. These four elements are fluorine—first isolated in 1886 by HENRI MOISSAN (1852–1907), at that time a Demonstrator at the École de Pharmacie, Paris—chlorine, bromine<sup>2</sup> and iodine.<sup>3</sup>

<sup>1</sup> From the Latin *muria*=brine.

<sup>2</sup> So called because of its powerful odour, somewhat resembling that of chlorine, the name being derived from the Greek βρωμος (brōmos), a stench. Bromine was discovered by the French chemist Antoine Jérôme Balard (1802–1876) in 1826.

<sup>3</sup> So called because it forms a beautiful violet-coloured vapour, the name being derived from the Greek ιοειδής (ioeidēs), violet coloured. It was first isolated in 1812 by a French saltpetre manufacturer, Bernard Courtois (1777–1838). Its elementary character was established by Gay-Lussac.

*Fluorine* is a gas which is exceedingly active chemically. Its compound with hydrogen, hydrogen fluoride (HF), is used both in the gaseous form and in solution (hydrofluoric acid) for etching glass.

*Bromine* is a deep reddish-brown coloured liquid obtained from the salts (bromides) present in the great deposits near Stassfurt in Germany, and in the brine in the Saginaw Valley, Michigan, U.S.A. It forms compounds similar to those formed by chlorine, *e.g.* hydrogen bromide (HBr), and potassium bromide (KBr), the last-mentioned salt being very largely employed for the production of silver bromide (AgBr), the light-sensitive salt of the photographic film.

*Iodine* is a very dark violet-coloured crystalline solid, which is obtained in small quantities from the ash of sea-weed (kelp), but is mainly obtained from crude Chile saltpetre, in which it occurs as sodium iodate ( $\text{NaIO}_3$ ). It dissolves in alcohol to form a brown-coloured solution—tincture of iodine—used for sterilising wounds. Traces of iodine can be detected by means of starch, with which it gives a deep blue colour. A complex compound of iodine—*thyroxine*—is present in small amount in the thyroid gland, and is essential to healthy growth. The chemical nature of thyroxine was determined in 1927 by the English chemists, C. R. HARRINGTON, Clinical Chemist, University College Hospital, London, and G. BARGER, Professor of Medical Chemistry, University of Edinburgh, who also succeeded in preparing it synthetically in the laboratory.

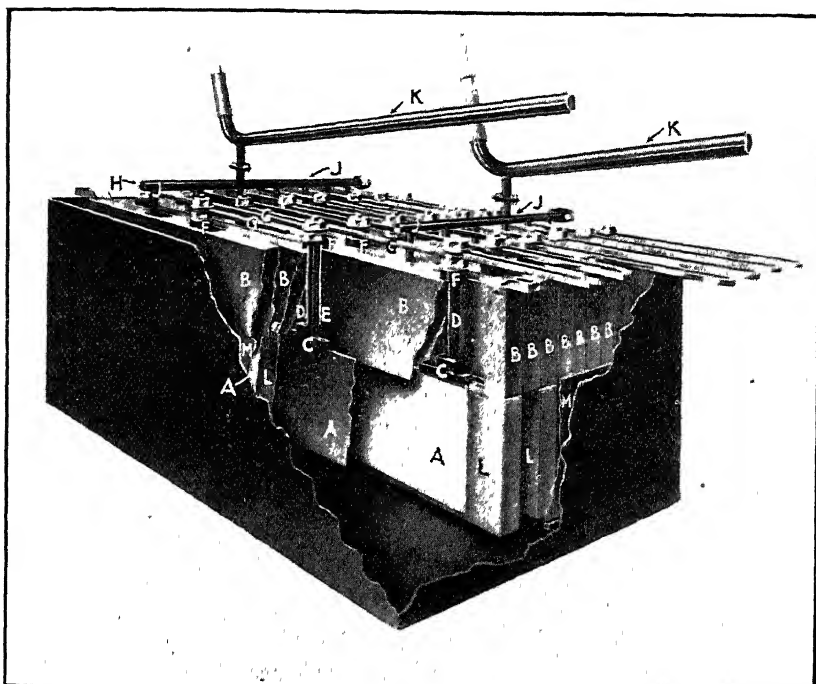
The four chemically related elements, fluorine, chlorine, bromine and iodine, are known as the *halogens*<sup>1</sup> or salt formers, because chlorine, the most important member of the group, gives rise to sodium chloride or common salt—salt *par excellence*.

Although in the electrolysis of solutions of sodium chloride the hydrogen which is produced must be considered as a by-product, and is sometimes wasted, the electrolytic process is also extensively used for the primary production of pure hydrogen and oxygen. In this case, a solution of caustic soda is generally employed as an electrolyte. When the electric current is passed through this solution, hydrogen is liberated at the cathode, owing to the reaction of the discharged sodium ions with the water, and oxygen is liberated at the anode, the discharged hydroxide ions reacting to form water and oxygen:  $4\text{OH} = 2\text{H}_2\text{O} + \text{O}_2$ . The electrolytic production of hydrogen is carried out, more especially, in Italy, France and Spain, in localities

<sup>1</sup> From the Greek *ἅλς* (hals), salt, and *γεννάω* (gennāō), I produce.

where electrical energy is obtainable at a low cost, and is used for the synthetic production of ammonia, etc.

In chemical industry, electrical energy is applied not only for the purpose of bringing about the decomposition of compounds, as in electrolysis, but also for the purpose of producing high temperatures. By means of the electric arc, for example, a temperature of about  $3000^{\circ}\text{C}$ . can, as has already been pointed



Knowles' cell for the electrolytic production of hydrogen and oxygen.

The electrodes, A, are separated by diaphragms of asbestos cloth, L, and are surmounted by metal boxes, B, in which the gases collect. From these boxes the gases pass by the pipes, J, to the off-take pipes, K.

out, be obtained, and this has been made use of for the preparation of phosphorus (p. 175), calcium carbide (p. 218) and other substances. The high temperatures which can now be produced economically by means of electricity have enabled chemists not only to advance to a fuller knowledge of substances and materials already known, but also to prepare others hitherto unknown.

As a direct result of the successful application of electricity to the production of high temperatures, we owe the very valuable

material known as *carborundum*, a compound of carbon and silicon, discovered by the American chemist, Dr. EDWARD G. ACHESON, in 1891. By heating a mixture of coke (carbon) and sand (oxide of silicon) to a high temperature in an electric furnace (Fig. 59), oxygen is removed by the carbon from its combination with silicon, and the latter then combines with the excess carbon

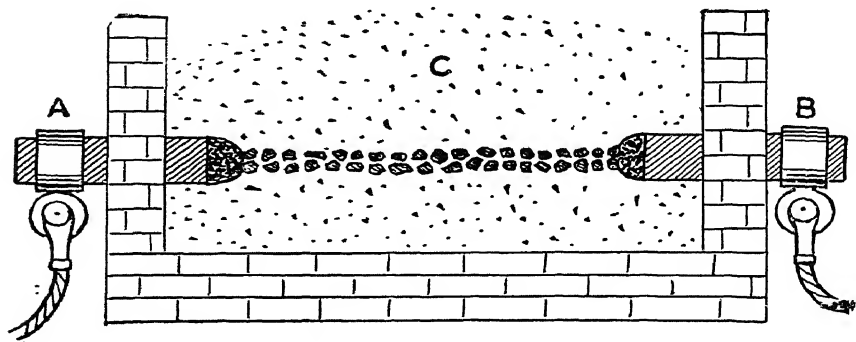


FIG. 59.—Carborundum furnace.

A core of granular graphite is raised to a white heat by a powerful current of electricity which passes between the graphite terminals, A and B. At the high temperature which is thereby produced, the carbon and sand of the surrounding mixture, C, react with formation of carborundum.

to form the crystalline compound, carborundum (silicon carbide):



Carborundum, which has a hardness approaching that of the diamond, is now produced in large quantities and used as a grinding or abrasive material. By reason of its very refractory character (it will withstand a temperature of  $2200^{\circ}\text{C}.$ , without undergoing change), it is also used for the protection of furnace walls and for other heat-resisting purposes.

Another very valuable abrasive and refractory material of which mention may be made, is *alundum* (alumina or aluminium oxide,  $\text{Al}_2\text{O}_3$ ), which is obtained by fusing purified bauxite (alumina) in an electric furnace.

## CHAPTER XVIII

### METALS AND THEIR PROPERTIES

**Metals in Antiquity.**—The history of the development of human civilisation has frequently been divided into three ages or epochs—the stone age, the bronze age and the iron age—according to the material most commonly and abundantly in use for the making of tools, implements and weapons of the chase or of defence. This view, which one finds expressed by the writers of antiquity, may be regarded either as purely conjectural or as the expression of a fact retained, in legendary fashion, in the memory of the race. However that may be, it is a view which is in harmony with the findings of archæology that, in the dawn of civilisation, flint and stone were employed by primitive man for the fashioning of tools, weapons and other articles, at a time when, as yet, copper, bronze and iron were unknown. Moreover, although it is not possible to fix with any degree of accuracy the dates at which the metals, copper and iron, were discovered, it is probable that copper and bronze were known and widely used for everyday purposes before man had learned how to extract iron from its ores and apply it to general use. This does not exclude the possibility, even the probability, that meteoric iron was known before that time—perhaps even as early as copper—and was used for the making of beads and other articles of adornment. But whatever the truth may be regarding the sequence of the different “ages,” there appears undoubtedly to have been much overlapping, so that, among certain races, iron was in common use at a time when, among other races, bronze or even stone was still generally employed. At the present day, one may perhaps say that we are still in the iron age, although, certainly, other metals are, year by year, finding an ever-extending application.

In Ancient Egypt, even before 1200 B.C., gold, silver, electrum (an alloy of gold and silver), copper, bronze, iron, lead, mercury, and, to some extent, antimony and tin, were known. Under the influence of Chaldean philosophy, the number of the metals was taken to be seven, and as they were thought to be affected

y and to derive their properties from the sun and planets, the names of these were applied to the metals. As Chaucer wrote : <sup>1</sup>

The bodies seven, eek, lo hem heer anon :  
 Sol gold is, and Luna silver we threpe ;  
 Mars iren, Mercurie quyksilver we clepe ;  
 Saturnus leed, and Juppiter is tyn,  
 And Venus coper, by my fader kyn.

Moreover, the astronomical signs used for the planets were employed to represent the metals, as shown in the following list :

Metal.	Planet	Sign.	Metal.	Planet.	Sign.
Gold	Sun	☉	Lead	Saturn	♄
Silver	Moon	☾	Tin	Jupiter	♃
Copper	Venus	♀	Quicksilver	Mercury	☿
Iron	Mars	♂			

Traces of these old designations are still met with, *e.g.* lunar caustic (silver nitrate), but of the old names only one remains in use, namely, mercury.

By the alchemists, metals were characterised as *noble* or *base*, according as they remained unchanged when heated in air (as in the case of gold and silver), or became oxidised and lost their metallic properties (as in the case of copper, lead, tin, etc.).

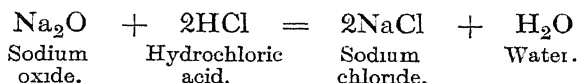
**What is a Metal?**—It has already been pointed out that chemists are wont to classify the elements into metals and non-metals ; and this grouping of the elements, although not always sharply defined, is at least convenient. Ordinarily, one thinks of a metal as being opaque and as showing, in the compact state, a lustre—the so-called metallic lustre. One thinks, also, of a metal as being a good or fairly good conductor of heat and electricity, and as being fusible, malleable and ductile. The alchemist, JABIR IBN HAYYAN or GEBER, in fact, gave as a definition of a metal : “ Metallum est corpus minerale fusibile et sub malleo ex omni dimensione extensibile.” These physical properties, however, serve by no means satisfactorily to define a metal or to distinguish it from a non-metal ; for not only does one find, among the different metals, very great variation in the value of any particular property, but some elements, universally regarded as non-metals, may show some at least of the properties which have just been mentioned as characterising the metals. Graphite, for example, is lustrous and a conductor of electricity.

If, however, one turns from the physical to the chemical properties, a sharper definition can be obtained. As has already

<sup>1</sup> Canon's Yeoman's Tale.

been pointed out, sulphur, phosphorus and carbon—substances which are regarded as non-metallic elements—yield oxides which unite with water to form *acids*. Sodium and calcium, however, which are regarded as metallic elements, yield oxides which have *basic* properties; that is to say, the oxides have the property of neutralising acids so as to form salts. *One may, therefore, define a non-metal as an element which gives rise only to an acid-forming oxide, or to acid-forming oxides; and a metal as an element which can give rise to a basic oxide.* The formation, also, of acid oxides by a metal is not excluded.

Moreover, since a basic oxide neutralises an acid and so gives rise to a salt, as represented, for example, by the equation :



and since, according to the Arrhenius theory of electrolytic dissociation, the salt is ionised into positively charged metal ion ( $\text{Na}^+$ ), and a negatively charged acid ion ( $\text{Cl}^-$ ), *one may also define a metal as an element which can give rise in solution to positively charged ions.* Thus, all those elements, gold, silver, iron, zinc, lead, etc., which we regard as metals, form positively charged ions in solution, whereas graphite (carbon), for example, which in some of its physical properties resembles the metals, does not do so.

**Metallurgy.**—With the exception of gold and the platinum metals (platinum, palladium, osmium, iridium), and, to a small extent, silver and copper, the different metals must be extracted by various metallurgical processes from naturally occurring compounds or *ores*. Of these compounds, the most important are oxides and sulphides, and, to a less extent, carbonates and silicates. These compounds do not occur pure in nature, but are frequently mixed with varying amounts of earthy impurities, *gangue*, most of which must be removed before the ore is subjected to further treatment.

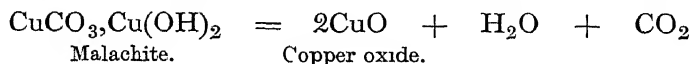
The “concentration” of the ore may be effected, in some cases, by grinding and shaking with water or “washing,” in order to remove the lighter earthy impurities; or a separation may be effected by means of magnets, owing to differences in the magnetic properties of the constituents. More recently, a process has been introduced known as the *flotation process*, which has shown itself to be of great utility in the case, more especially, of sulphide ores, such as those of copper, zinc and lead. The crude ore, finely ground, is introduced into a large

tank containing water (rendered slightly acid or alkaline), and certain kinds of oil, such as pine oil or eucalyptus oil. Air is then blown through the mixture and a thick froth or foam is formed. Since the sulphide particles are wetted by the oil rather than by the water, they adhere to the oily walls of the air-bubbles, whereas the earthy particles, being preferentially wetted by the water, sink to the bottom of the water layer. The layer of froth, carrying with it the particles of metal sulphide, is then skimmed off.

The "concentrates," or concentrated ores, are then subjected to suitable metallurgical treatment; and it is of interest to note that many of the processes now in use for the treatment of ores, were tested and developed by the metallurgists of the Middle Ages. For a knowledge of these processes, as they were carried on in the sixteenth century, we are indebted to the excellent book, *de re metallica*,<sup>1</sup> by the German schoolmaster and physician, GEORG BAUER, better known under the latinised form of his name, GEORGIUS AGRICOLA (1494-1555).

Although it is not possible to discuss the matter in detail here, it may be said that, most generally, the treatment to which the ores are subjected consists in *smelting*, or heating the ore to a high temperature along with substances which will combine with any earthy impurities which may be present and at the same time set free the metal from the compound in which it is present in the ore. When the ore is an oxide—for example, hæmatite,  $\text{Fe}_2\text{O}_3$ —it is reduced to the metallic state by smelting with coal or coke. The carbon combines with the oxygen of the ore to form carbon monoxide, and the metal is set free.

When the ore is not an oxide, it is first converted to an oxide by preliminary treatment. Thus, in the case of a carbonate, such as malachite or basic copper carbonate,<sup>2</sup>  $\text{CuCO}_3, \text{Cu}(\text{OH})_2$ , the ore is heated in order to drive off water and carbon dioxide:



The oxide so obtained is then reduced by heating with coke.

When the ore is a sulphide, it is heated in the air, or "roasted," as it is said. The oxygen of the air unites with the sulphur of the sulphide to form sulphur dioxide (which can be used, as we shall learn later, for the manufacture of sulphuric

<sup>1</sup> This book was published posthumously in 1556. An excellent English translation by H. C. and L. H. Hoover was published in 1912.

<sup>2</sup> Malachite is called a *basic* carbonate because it is a compound of the normal carbonate,  $\text{CuCO}_3$ , with the base,  $\text{Cu}(\text{OH})_2$ .



acid), and combines with the metal to form an oxide. The oxide can then be reduced as before by means of coke.



Sixteenth-century furnace for smelting iron ores.

(From Agricola: *de re metallica*.)

A workman standing on the steps, B, is emptying into the furnace a mixture of ore, C, and coal, D.

Other processes are also in use for the extraction of metals, and to some of these reference will be made in due course.

**The Structure of Metals.**—A metal which has solidified from the molten state has a crystalline structure, and it is on the nature and development of this that the properties of the metal largely depend.

Every one is familiar with the fact that the surface of galvanised iron—that is, iron coated with a layer of zinc which has solidified from the molten state—shows a fern-like or leaf-like appearance (Fig. 60), somewhat similar to what is seen when



(Courtesy Prof. C. H. Desch.)

FIG. 60.—Leaf-like crystals of zinc.

moisture is frozen on the window-pane. This fern-like or dendritic appearance (p. 127), is an indication of the crystalline structure of the zinc. A similar appearance is obtained in the case of tin, when dilute acid, or some other etching liquid, is brushed over the surface of the metal.

Still more distinctly does the crystalline structure of a metal appear when a polished surface of the metal, after being treated with a suitable etching liquid, is examined under the microscope. In this case, the crystals are seen as a number of polygonal grains, closely packed together (Fig. 61).

The method of microscopic examination of the structure of metals, although previously used by others, is almost entirely due to HENRY CLIFTON SORBY (1826–1908), of Sheffield, a scientific worker of private means who, in 1863, devised the technique for the preparation and examination of metal sections. This branch of study, known as *metallography*, is of the highest importance, for it enables one to correlate the changes which take place in the physical properties of metals with the changes in crystalline structure; and it gives guidance, also, in the production of a suitable crystalline texture.

In recent years, pure metals and alloys have also been subjected to examination by means of X-rays, and a fuller knowledge

of their crystalline structure and of the spacing of the atoms in the crystals has thereby been obtained.

When copper is used as a conductor of electricity, it is of the highest importance that it be as pure as possible; but for other purposes, where the metal is subject to wear and tear, pure copper is too soft. If the copper is mixed even with a small amount of tin, however, a metal of much greater hardness and resistance to wear is obtained, as was found by the craftsmen of antiquity who discovered bronze. In the case of other metals, also, a very great variation of properties can be brought

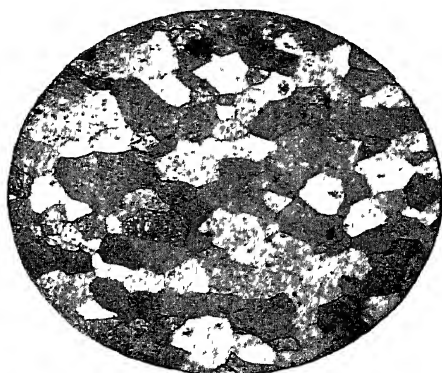



FIG. 61.—Crystalline structure of metals.

(From Evans' *Metals and Metallic Compounds*, by permission of Messrs. Edward Arnold & Co.)

about by the addition of different amounts of one or more metals; and in this way very many *alloys* possessing properties of the highest value have been produced. These alloys are, in some cases, merely heterogeneous but close-grained mixtures of the metals; but in other cases, they are compounds. In still other cases, they are homogeneous mixtures or *solid solutions*. 

Owing to the fact that the crystalline texture may be considerably altered by mechanical stress and by alternate heating and cooling, the properties of an alloy depend not only on the composition but also on the mechanical and thermal treatment to which it is subjected. Examples of such behaviour will be given in the following chapter.

## CHAPTER XIX

### METALS AND ALLOYS

#### GOLD, SILVER AND PLATINUM

THESE three precious metals are largely used for currency, jewellery and scientific purposes. All occur in the free state, and silver and platinum also occur as compounds associated with other metals.

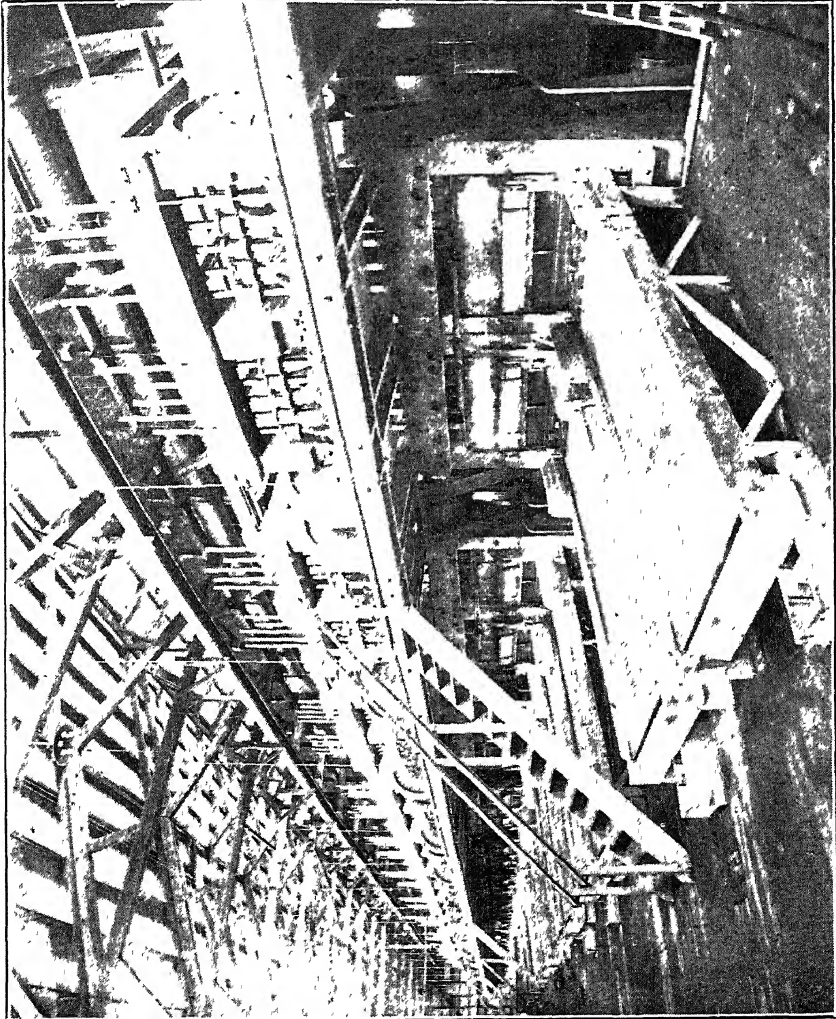
**Gold**, probably, was the first metal to become known to man, and its natural beauty and the ease with which it can be worked must have attracted primitive man, as it has attracted men throughout all ages, and have led to its use, at an early period, for purposes of personal adornment. The beautiful gold jewellery—bracelets, rings, etc.—to be seen in the Museum at Cairo, show that the use of gold for ornamental purposes was already well known in Egypt as early as 4000 B.C. Egypt, indeed, became noted throughout the Ancient World for its wealth in gold: "The gods have done well in making gold as plentiful as dust in the land of Egypt," wrote<sup>1</sup> Dusratta, King of Mitani, to Amenophis III, King of Egypt, about 1400 B.C.

Gold is very widely distributed and has been found, in larger or smaller amounts, in many parts of the world. In the first half of the nineteenth century, the gold mines of the Urals produced almost all the world's supply; but with the opening up of the alluvial deposits and gold mines of California in 1848-49, of Australia in 1851, and of the Transvaal (South Africa) in 1873, the Ural mines became of little importance. In 1927, the world production of gold amounted in value to £82,000,000, and of this about 50 per cent. was produced by the Transvaal, about 21 per cent. by other parts of the British Empire (Australia, Canada, etc.), and about 11·5 per cent. by the United States.

Although much gold has been obtained from sands and alluvial deposits, most of the gold is now isolated from gold-bearing rocks. The auriferous rock is crushed by means of "stamps," or heavy steel pestles from 1½ to 2 tons in weight, and

<sup>1</sup> Tell-el-Amarna Tablets.

ground in rotary mills. The finely crushed material is washed over large plates covered with corduroy cloth, which retains the heavy gold particles. The gold particles are then shaken in



Stamps for crushing gold-bearing rock.

closed vessels with mercury, which dissolves the gold—a fact well known to Pliny in the first century. The mercury-gold amalgam is then distilled, when the mercury passes off and leaves the gold behind. The sands from which the gold has for the most part been separated are then treated with a solution of

potassium cyanide, or of the cheaper sodium cyanide, in order to dissolve the gold which has escaped removal. From the cyanide solution, the gold can be recovered by the addition of zinc. This causes the gold to separate out, while the zinc itself passes into solution.

Gold is a very malleable metal which can be rolled or beaten out into leaves one ten-thousandth of a millimetre (one two-hundred-and-fifty-thousandth of an inch) in thickness. These leaves are so thin as to be translucent, the light which passes through having a green colour. Gold can also be drawn into wires of extreme tenuity. The purity or fineness of gold is generally expressed in carats, pure gold having a fineness of 24 carats. Since pure gold is too soft for use, it is alloyed or mixed with silver or copper. British currency gold has a fineness of 22 carats, and consists of a mixture of 22 parts of gold with 2 parts of other metals, or, 91.67 per cent. of gold, 2 per cent. of silver and 6.33 per cent. of copper. In Australia, silver is used in place of copper. In the United States, France and Germany, currency gold consists of 90 per cent. of gold and 10 per cent. of other metals. The finest quality of jewellery gold is 18 carat gold, or a mixture of 18 parts of gold with 6 parts of other metals (75 per cent. of gold, 12.5 per cent. of silver and 12.5 per cent. of copper); but lower qualities, especially 15 and 9 carat gold, are also employed.

Gold is not readily attacked by any single acid, and the most convenient solvent for the metal is the *aqua regia* of the alchemists, a mixture of nitric and hydrochloric acids. From a solution in *aqua regia* there crystallises out the yellow salt known as "gold chloride," which is widely used for the "toning" of photographic prints.<sup>1</sup> In the toning process, the silver particles forming the image are replaced by particles of gold.

**Silver** is a metal which, like gold, occurs native, more especially in Ontario, Canada; but it is generally found as a sulphide associated with lead or copper, and is produced mainly in Mexico, the United States, South America and Canada. Most of the silver is produced at the present day as a by-product of the extraction of lead and copper from their ores.

Silver, although known in pre-dynastic times in Egypt, was a rarer and more costly metal than gold until about 1500-1400 B.C. It has long been prized as a jewellery metal on account of its appearance, and it was used for the making of coins as early as the ninth century B.C., by the Æginetans, under Phidon,

<sup>1</sup> The salt has the composition represented by the formula,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ .

King of Argos. Its use as a currency metal is now very widespread. Formerly, British sterling silver was an alloy containing  $7\frac{1}{2}$  per cent. of copper, while the silver coinage of the United States contains 10 per cent. of copper. Now, however, sterling silver contains only 50 per cent. of silver, and is alloyed with 40 per cent. of copper, 5 per cent. of nickel and 5 per cent. of zinc.

Silver is, next to gold, the most malleable and ductile metal ; and it is the best conductor of heat and electricity.

Silver does not combine with oxygen at the ordinary or even at a higher temperature, and does not, therefore, tarnish when exposed to pure air. The tarnishing which takes place when silver is exposed to the air, especially of large towns, is due to the presence of sulphur compounds in the air and the formation of silver sulphide. Similarly, so-called "oxidised silver" is not oxidised at all, but "sulphidised" by treatment with a solution of an alkaline sulphide. A film of dark silver sulphide is thereby formed on the surface of the metal. An alloy of silver and copper, containing 92.5 per cent. of silver and a little antimony, resists the blackening action of sulphur compounds in the air. It is used, under the name of "stainless silver," for the manufacture of ware.

Silver dissolves readily in nitric acid, and from the solution the white crystalline salt, *silver nitrate* ( $\text{AgNO}_3$ ) or "lunar caustic," can be obtained. It is used in medicine as a cautery. A solution of silver nitrate, when applied to the skin, gives a black stain, owing to the production of metallic silver. For the same reason, a solution of silver nitrate may be used as a *marking-ink* for linen, etc. The silver nitrate is reduced and metallic silver deposited on the linen.

On account of the fact that they are acted on by light, the compounds of silver with the halogens, more especially silver chloride ( $\text{AgCl}$ ) and silver bromide ( $\text{AgBr}$ ), are extensively employed in photography. These compounds separate out as sparingly soluble precipitates when a chloride (*e.g.* sodium chloride) and a bromide (*e.g.* potassium bromide) are added to a solution of silver nitrate.

**Platinum**, now the costliest of all metals, first became known in Mexico about 1558, and was called by the Spaniards, *platina*, a diminutive form of *plata*, silver. It was first brought to Europe in the eighteenth century. From about 1824 down to the time of the Russian Revolution, most of the world's supply of platinum was obtained from Russia, where the metal was found in the region of the Ural Mountains. The supply from this source,

however, has greatly diminished, and the metal is now derived to a large extent from the Republic of Colombia, South America, and from the province of Ontario, Canada. In 1925, extensive deposits of platiniferous ores were discovered in the Transvaal.

Platinum is a malleable and ductile metal, much valued as a jewellery metal for the setting of diamonds and other gems; and it is largely used in chemical laboratories on account of its high melting-point and its freedom from attack by chemicals. It finds, also, considerable application in industry as a catalyst, as will be discussed in the sequel.

Owing to the fact that platinum expands and contracts with change of temperature at nearly the same rate as glass, a wire of this metal can be melted into glass, and the latter does not crack on cooling. For this reason, platinum wire used to be employed in making connection between the filament of an electric incandescent lamp and the fittings outside. Owing to its present high price, however (about £17 per ounce troy), platinum is no longer used for this purpose, its place being taken by the nickel-iron alloy *platinite* (see later). When used for this purpose, the platinite is coated with a thin layer of copper, to which the glass adheres. It is then known as "red platinum." The saving effected by the use of platinite amounts to about £1,000,000 per annum.

### IRON AND STEEL

No metal, it may be said, has played a part of such importance in the advance of civilisation as has the metal iron. Although meteoric iron appears to have been known in Egypt in pre-dynastic times—prior to the fourth millennium B.C.—a knowledge of how to extract the metal from its ores must have come only at a much later time; when and where, cannot be stated with any degree of certainty. It is, however, believed by some that the extraction of iron from its ores was a Hittite discovery, and that the production of iron was first established in the district to the south-east of the Euxine. By 1300 B.C., in any case, iron, although still very valuable, was well known, and about that time an iron sword was sent by a Hittite king to Rameses II, King of Egypt. Even as early as the fourth century B.C., "damascened" steel was being produced in Damascus; and in the reign of Augustus, in the first century B.C., the "Noricus ensis" (Noric sword), made from steel produced in Illyria, was no less famous than were, at a later date, the swords of Toledo.



**Extraction of Iron from its Ores.**—Although the element iron forms about 5 per cent. of the solid crust of the earth, it occurs, with the exception of small quantities of meteoric iron, only in the form of compounds, more especially with oxygen and with sulphur. Of these, the most important are *hæmatite*<sup>1</sup> ( $\text{Fe}_2\text{O}_3$ ),—the presence of which gives a red colour to rocks and soil,—*limonite*, a hydrated oxide ( $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$ ), and magnetic iron ore or *magnetite* ( $\text{Fe}_3\text{O}_4$ ). Iron pyrites or ferric sulphide ( $\text{FeS}_2$ ) is a familiar brass-like mineral, sometimes called “fool’s gold.” It is never used for the production of iron, but large quantities are employed in the manufacture of sulphuric acid.

Various red and brown pigments, *ochres*, are prepared from hæmatite and limonite.

The ores which are mainly employed for the production of iron are the oxides—hæmatite, limonite and magnetite—and the carbonate ( $\text{FeCO}_3$ ), known as spathic iron ore or *siderite*. The ores are subjected to a preliminary process of calcination in order to drive off water and to convert the carbonate to oxide. The extraction of the metal is carried out in the blast furnace, a tall structure with a roughly egg-shaped interior (Fig. 62). After fires have been lit and the furnace has been heated up, a mixture of ore, coke (or coal) and limestone (calcium carbonate) is introduced from the top, and a blast of hot air is blown in through pipes or “twyers” (French, *tuyères*), at the bottom of the furnace. In this way, a high temperature is produced; the coke burns and gives rise to carbon dioxide, and this gas, in contact with the red-hot coke, passes into carbon monoxide. The carbon monoxide ascends through the hot mass, combines with the oxygen of the iron ore and so sets free the metal. At the high temperature of the furnace, the metal melts and flows down to the bottom, and at the same time the lime, formed by the decomposition of the limestone, com-

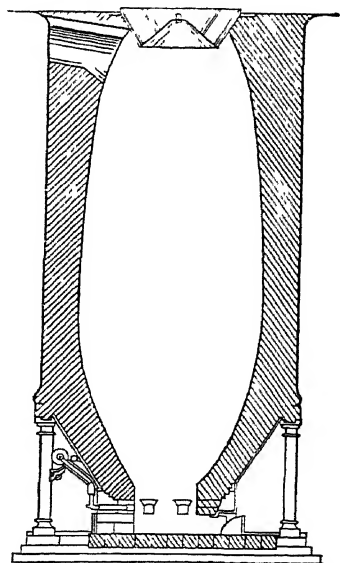


FIG. 62.—Section of blast-furnace (diagrammatic).

<sup>1</sup> So called because “seeming as if formed of concremented blood” (Theophrastus), from the Greek *αἷμα* (*haima*), blood.

bines with the silicates added to or present as impurities in the iron ore, to form a glass-like material or slag. This likewise flows in the molten state to the bottom of the furnace, where it floats on the surface of the molten iron. From time to time, the slag is removed and the molten iron run off into moulds, where it solidifies and forms *pig iron*.

The slag obtained from the blast furnace is used in the manufacture of Portland cement, the production of which will be discussed at a later point. The carbon monoxide, also, which is drawn off in large quantities from the top of the blast furnace is made use of, partly for burning in furnaces to heat the air of the blast, and partly for the production of power in gas engines.

**Cast Iron, Wrought Iron and Steel.**—Pure iron is never used industrially, and all commercial forms of iron are mixtures of iron with larger or smaller amounts of other substances. The three main kinds of commercial iron are *cast iron*, *wrought iron* and *steel*, and of these, the first is the least pure form of iron. Cast iron is essentially the metal as it comes from the blast furnace, and contains generally from 2 to 5 per cent. of carbon, much of it in the form of graphite, together with other impurities, such as silicon, sulphur and phosphorus, in amounts depending on the ore employed. It is a hard but brittle form of commercial iron.

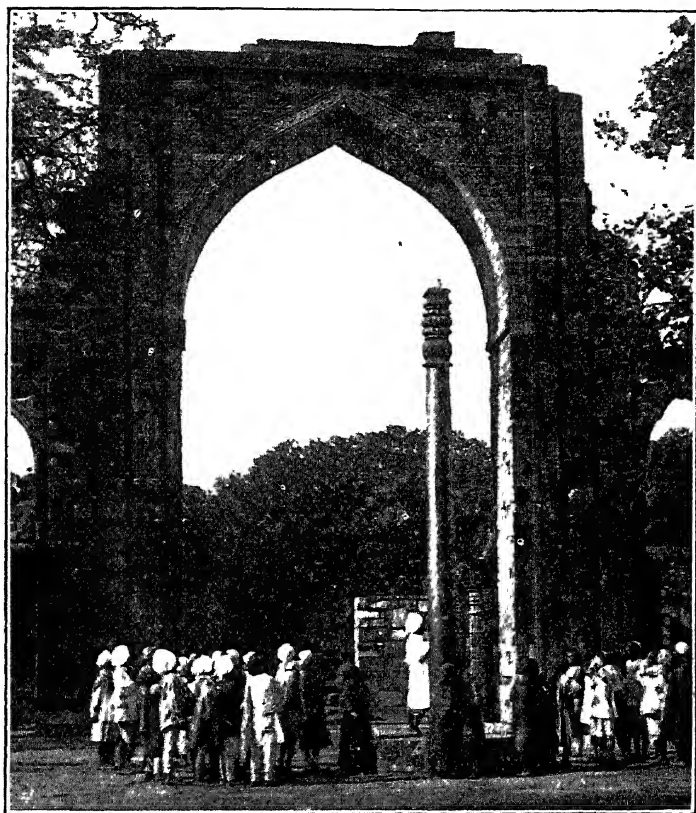
Ordinary *cast iron* is readily attacked by dilute hydrochloric and sulphuric acids, but the rate of attack can be reduced to a very considerable extent by increasing the proportion of silicon. Thus, ware made of cast iron containing from 12 to 19 per cent. of silicon (*e.g.* tantiron, duriron, ironac, narki), is so acid-proof that it can be used for the evaporation of sulphuric acid. Such cast iron, however, is extremely brittle.

*Wrought iron*, the purest form of iron used industrially, is obtained by strongly heating pig iron in a furnace along with hæmatite or magnetite. These oxides oxidise the carbon and silicon, as well as any phosphorus and sulphur which may be present. Wrought iron is soft and fibrous in structure, and is also tough and malleable, so that it can readily be worked even at the ordinary temperature. A pillar of wrought iron, twenty-four feet in length, stands in the Mosque of the Kutub, near Delhi, and dates from the fourth century.

*Steel*, by far the most important form of commercial iron, is not a definite substance; there are many different kinds of steel, all of which are alloys of iron with other substances. Ordinary steels are alloys of iron and carbon, the amount of

carbon varying from 0.1 to 2.0 per cent. The carbon is present in the form of a compound of iron, known as cementite,  $\text{Fe}_3\text{C}$

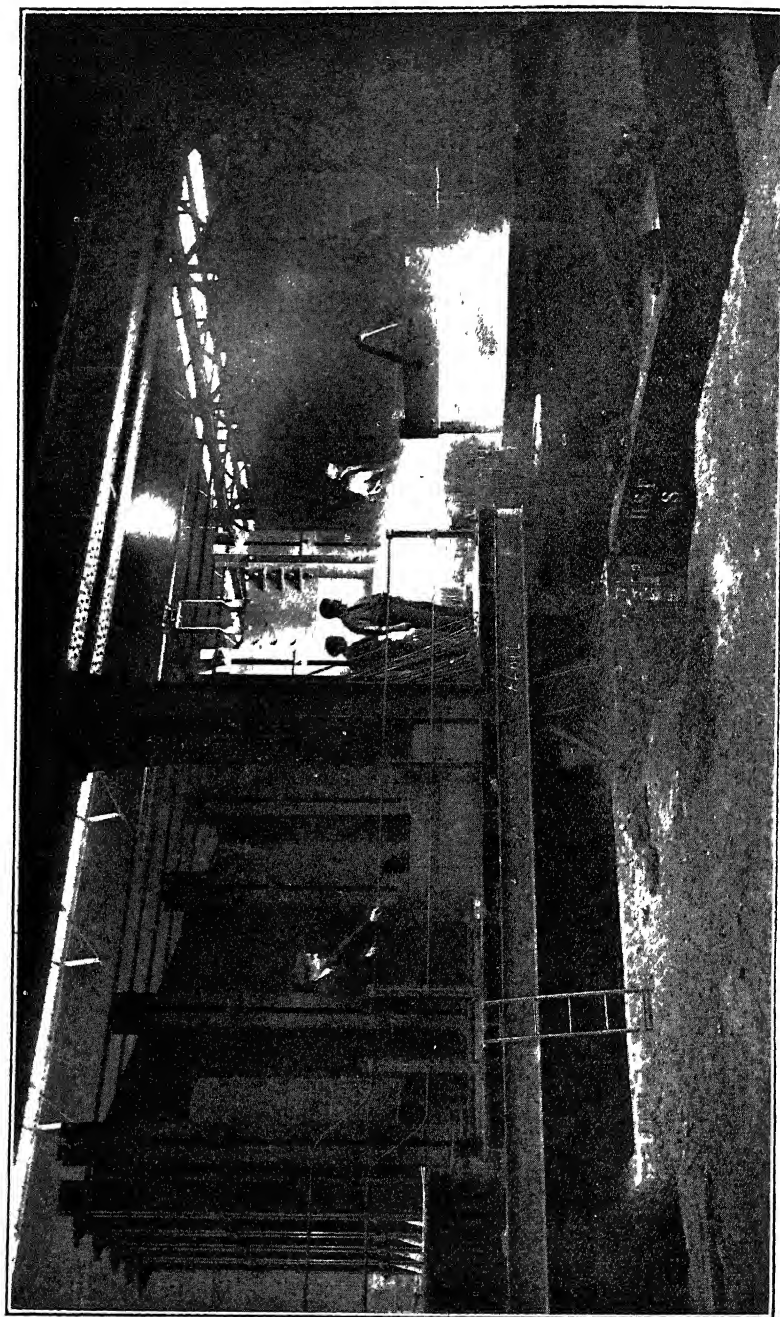
Steel is produced by the Bessemer or, generally, by the open-hearth process, the aim in either case being to remove, by burning or oxidation, the impurities present in pig iron, and more especially the sulphur and phosphorus, the presence of which is



*Photo: E. N. A.*

Pillar of wrought iron near the Kutub Minar, Delhi.

very detrimental to the steel. In the Bessemer process, introduced by the English ironmaster, Sir HENRY BESSEMER, in 1855, the oxidation is effected by blowing air through the molten metal; and in the open-hearth process, introduced by Sir WILLIAM SIEMENS in 1863, the oxidation is effected by the addition of oxide of iron or hæmatite. When phosphorus is present in the pig iron, the furnace is lined with magnesite



Tapping a Siemens-Martin steel furnace.

(Courtesy Sir Robert A. Hadfield, Bt.)

(magnesium carbonate), or with dolomite (double carbonate of calcium and magnesium), with which the oxidised phosphorus combines to form a phosphate known as *basic slag*. This is largely employed as a phosphatic manure in agriculture. The introduction of a basic lining to the furnace is due to SIDNEY GILCHRIST THOMAS (1850–1885), a magistrate's clerk in London, and has made available for steel manufacture hundreds of millions of tons of ore.

Besides possessing a much greater tensile strength than cast or wrought iron, steel is characterised by the fact that it can be hardened by heating to a fairly high temperature and then cooling in oil or in water. The process is known as *tempering*, and the temper (hardness, elasticity, etc.) produced in the steel depends not only on the composition but also on the temperature to which it is heated and the rate at which it is cooled down. According to the treatment employed, the highly elastic steel of the watch-spring or the hard steel of the cutting tool can be obtained.

Following on the pioneering work more especially of Sir ROBERT A. HADFIELD, in the 'eighties of last century, the effect of adding other substances to steel has been the subject of intensive investigation by metallurgical chemists, and, as a result, many new steels, possessing distinct and valuable properties, have been introduced into the service of man. The addition of chromium, for example, gives hardness to steel, and thus, by the addition of about 2 per cent. of chromium one obtains *chrome steel*, which is employed for steel tyres, for rock-crushing machinery and for armour plate. By adding a small amount of nickel to the chrome steel, greater elasticity is given. "Stainless steel," which does not rust or tarnish in contact with food or fruit acids, is a steel containing from 12 to 15 per cent. of chromium. Steel containing from 10–15 per cent. of chromium and from 1–3 per cent. of nickel is highly resistant to the corrosive action of sea-water, acids, etc.

Addition of nickel to steel imparts hardness and elasticity, and *nickel steel* is therefore used for armour plate, propeller shafts, etc. When the percentage of nickel is greatly increased, steels having very special and valuable properties are obtained. Thus, *invar*, a steel invented in 1896 and containing 36 per cent. of nickel and only 0·2–0·5 per cent. of carbon, has a negligible coefficient of expansion throughout the ordinary range of temperature variation, and is therefore used for the manufacture of measuring rods, surveyor's tapes, instruments of precision and the pendulums of clocks. A similar alloy, *elinvar*,

is used for the balance spring of watches, because its coefficient of elasticity and therefore the control which the spring exerts, do not alter with the temperature. *Platinite*, similarly, is a nickel steel containing 46 per cent. of nickel. Its coefficient of expansion, which may be varied by slightly varying its composition, is practically the same as that of glass, and wires of platinite may therefore be sealed into glass. The invention of these three nickel steels we owe to CHARLES EDOUARD GUILLAUME, Director, since 1915, of the *Bureau International des Poids et Mesures*, at Sèvres, who was awarded the Nobel Prize for Physics in 1920.

During his investigations into the properties of manganese steel, carried out in the 'eighties of last century, Sir Robert A. Hadfield discovered that when the proportion of manganese, normally present in small amounts in all steels, is increased to from 9 to 14 per cent., a very hard, tough steel is obtained, which is extensively used for rock-crushing machinery, for switch-points on railways, and for other purposes where a very hard-wearing metal is required. It was also used for breastplates and steel helmets during the Great War.

The properties of an alloy, it has been pointed out, depend not only on the composition but also on the thermal or mechanical treatment to which the alloy is subjected. This is well illustrated by the behaviour of manganese steel. When heated and rapidly cooled, manganese steel is tough, ductile and non-magnetic: but if "annealed" by more or less prolonged heating and slow cooling, it becomes hard, brittle and magnetic.

In the production of the famous "Damascus steel," also, one has an illustration of the effect of heat and mechanical treatment. When a carbon steel containing, say, 1.6 per cent. of carbon, solidifies, cementite—a very hard and brittle compound of iron and carbon—crystallises in the form of needles which render the mass brittle and unforgeable (Fig. 63). If this steel be heated repeatedly to a bright red heat and hammered, the metal becomes more pliable and, at last, the very strong but pliable Damascus steel, capable of taking a very keen edge, is obtained. Microscopic examination reveals that as a result of the mechanical treatment of the red-hot steel, the cementite needles pass into a quasi-liquid state, lose their sharp outlines and break up into drops; and the drops of cementite are dispersed throughout the steel (Fig. 64), rendering the steel very hard and enabling it to take a very keen edge. On polishing the surface of the metal and washing it with a weak acid solution, the wavy markings, due to rows of cementite particles and

characteristic of Damascus steel, are revealed (Fig. 65).<sup>1</sup> The process outlined above is also made use of in the production of razor blades.



FIG. 63.—Steel with needles of cementite.

(From Belaiew's *Crystallisation of Metals*, University of London Press, Ltd.)

<sup>1</sup> How keen was the edge which could be obtained with Damascus steel is illustrated by the feats of swordsmanship described by Sir Walter Scott in *The Talisman*, Chap. 27. There we read that Saladin, having placed a cushion of silk and down upright on one end, "unsheathed his scimitar, a curved and narrow blade, which glittered not like the swords of the Franks, but was, on the contrary, of a dull blue colour, marked with ten millions of meandering lines. . . . Wielding this weapon . . . he drew the scimitar across the cushion, applying the edge so dexterously and with so little apparent effort, that the cushion seemed rather to fall asunder than to be divided by violence."



As a cutting tool, ordinary high-carbon steel is quite satisfactory as long as the work is carried out at such a rate that the

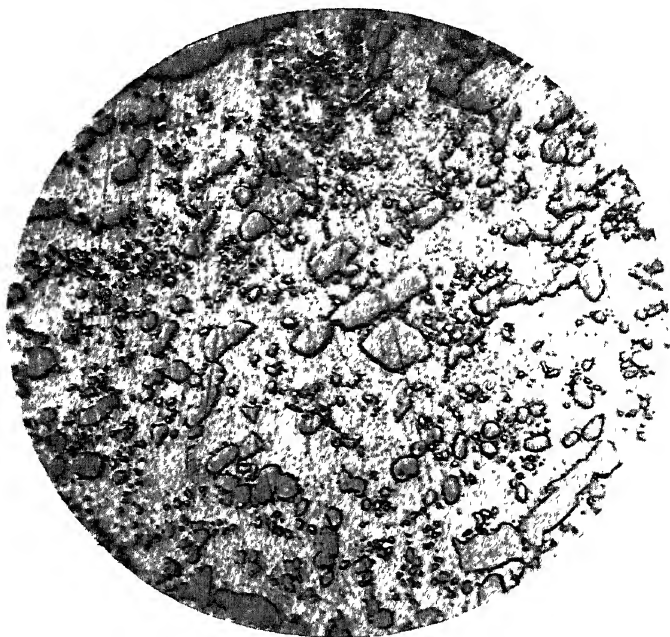


FIG. 64.—Steel with needles of cementite, after being worked.  
(From Belaiew's *Crystallisation of Metals*, University of London Press, Ltd.)

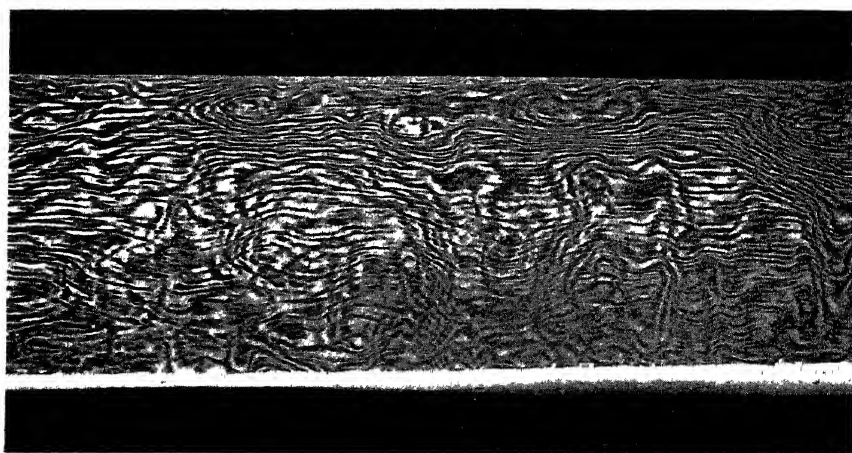


FIG. 65.—Damascus steel.  
(From Belaiew's *Crystallisation of Metals*, University of London Press, Ltd.)



temperature does not greatly rise, but it is useless for the high-speed cutting of metals, when the cutting tool may become red hot. Under these conditions, ordinary steel speedily loses its temper. It was, however, found that by the addition of tungsten or of molybdenum to a chrome steel, an alloy was obtained which retained its temper and hardness even at a red heat. Such high-speed tool steel, which contains, say, 0.6 per cent. of carbon; 4 per cent. of chromium, 14–20 per cent. of tungsten (or 5–6 per cent. of molybdenum), and sometimes also about 1 per cent. of vanadium, is therefore a material of the very highest value in modern engineering practice.

When exposed to moist air, iron readily undergoes oxidation or rusts. When used, therefore, in constructional work, protection of the metal by frequent painting is necessary. In other cases, the metal may be coated with zinc (galvanised iron) or with tin (tin plate).

**Ferrous and Ferric Salts.**—Iron readily reacts with dilute sulphuric and hydrochloric acids and gives rise to two series of salts, the ferrous salts (*e.g.* ferrous sulphate,  $\text{FeSO}_4$ ), and the ferric salts (*e.g.* ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , and ferric chloride,  $\text{FeCl}_3$ ), which may be regarded as derived from ferrous oxide ( $\text{FeO}$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ), respectively. The ferrous ion carries two charges of electricity ( $\text{Fe}^{++}$ ), and the ferric ion carries three ( $\text{Fe}^{+++}$ ).<sup>1</sup>

*Writing ink* is prepared by the addition of a solution of ferrous sulphate and gum to a decoction of nut-galls, in which gallo-tannic and gallic acids are present. On shaking with air, the white ferrous gallo-tannate and gallate are oxidised to the black ferric salts. In the presence of gum, the finely divided solid remains uniformly distributed as a colloidal suspension.

The fact that certain ferric salts are reduced to ferrous salts when exposed to light is made use of by engineers and others for the reproduction of line drawings. When paper, coated with a mixture of ammonium ferric citrate and potassium ferricyanide, is exposed to light under a black-line drawing, the ferric citrate is reduced to ferrous citrate, except where it is protected by the inked lines. If the paper, after exposure, is placed in water, the potassium ferricyanide reacts with the ferrous salt to give a blue colour (Prussian blue), whereas with the unaltered ferric salt it gives a soluble brown compound. On washing the sheet, therefore, this compound and the excess

<sup>1</sup> The termination *-ous* (*e.g.* ferrous) is applied to those compounds in which the metal has the lower valency; and the termination *-ic* (*e.g.* ferric) to those in which the metal has the higher valency.

of unaltered salts are removed, and one obtains a "blue print" reproduction of the original drawing, consisting of white lines on a blue ground.

### NON-FERROUS METALS AND ALLOYS

**Copper.**—Copper is, of all the non-ferrous metals, the most important and most widely used. It is, as has been pointed out, one of the metals with which man earliest became acquainted, and the copper mines of Sinai were worked as early as 5000 B.C. Helmets of copper, also, were worn by the warriors of the Sumerian City States as early as 2700 B.C. The name, copper, is derived from the Latin, *æs cyprium*, later, *cuprum*, because in Roman times it was largely obtained from the island of Cyprus.

Although copper occurs native, more especially in the region of Lake Superior, it is mainly from its compounds, the sulphide and the carbonate, that the metal is at present extracted; but in Chile, high up in the Andes, in what is reputed as being the largest known deposit of copper ore in the world, the sulphide has been largely converted to a sulphate. This ore has, however, not yet been exploited.

The chief industrial use of copper, of which the United States are the largest producers, is for the construction of wire and cable for the conduction of electricity; and since the conductivity, which is inferior only to that of silver, is greatly diminished even by small amounts of impurity, the metal as extracted from its ores must be refined or purified. This is now carried out by electrolysis (p. 266).

The crude copper, obtained by smelting its ores, contains a number of impurities, among which are silver and gold, sometimes in not inconsiderable quantities. This crude copper, cast into plates, is made the anode in a bath of copper sulphate solution, while a thin plate of pure copper is made the cathode. When the electric current is passed, copper is deposited in a pure state on the cathode, from which it can afterwards be readily stripped, whereas the copper of the anode passes into solution by combination with the sulphate ions which are discharged at the anode. Some of the impurities present in the copper may also dissolve and accumulate in the solution; other impurities, however, such as silver and gold, do not dissolve, but fall to the bottom of the bath as a slime or mud, known as the "anode mud," from which the valuable metals are extracted by suitable methods.

By this simple process, the purest commercial copper, so

called "electrolytic copper," is obtained, and is largely used for electrical purposes.

**Copper Alloys.**—In association with other metals, copper forms a number of alloys, some of which, the *brasses*, find a very wide-spread use. Brass is an alloy of copper and zinc, and brasses with different properties are obtained by varying the proportions of the two metals. Brasses containing about 30 per cent. of zinc are among the most important, and are used for castings and for cartridge cases. A brass containing 40 per cent. of zinc and known as *Muntz metal*, is used in sheathing ships on account of its resistance to corrosion. *Dutch metal* is an alloy containing about 20 per cent. of zinc.

Brass and certain other alloys which have been subjected to mechanical stress by being hammered, drawn or pressed, are liable to undergo what is called "season cracking." Thus, hard-drawn tubes, cartridge cases, etc., may crack some time after they have been made, more especially when exposed to an atmosphere in which traces of ammonia are present (Fig. 66). The liability to crack may, however, be removed by heating the metal to a temperature of 200°–300° C. At this temperature, the internal stresses are relieved, but the hardness of the metal is not destroyed.

Brass hardened with nickel—that is, an alloy of copper, nickel and zinc—is used under the name of *white metal* or *German silver*, as a basis for silver-plated ware.

**Bronzes**<sup>1</sup> are alloys of copper and tin, but they sometimes also contain zinc. *Gun metal* is a bronze containing from 8 to 12 per cent., and *bell metal* a bronze containing from 12 to 24 per cent. of tin. Bronze coinage contains 4 per cent. of tin and 1 per cent. of zinc; while *phosphor-bronze*, which is widely used for taps, valves, etc., where corrosion has to be avoided, contains varying proportions of copper, tin, lead and phosphorus.

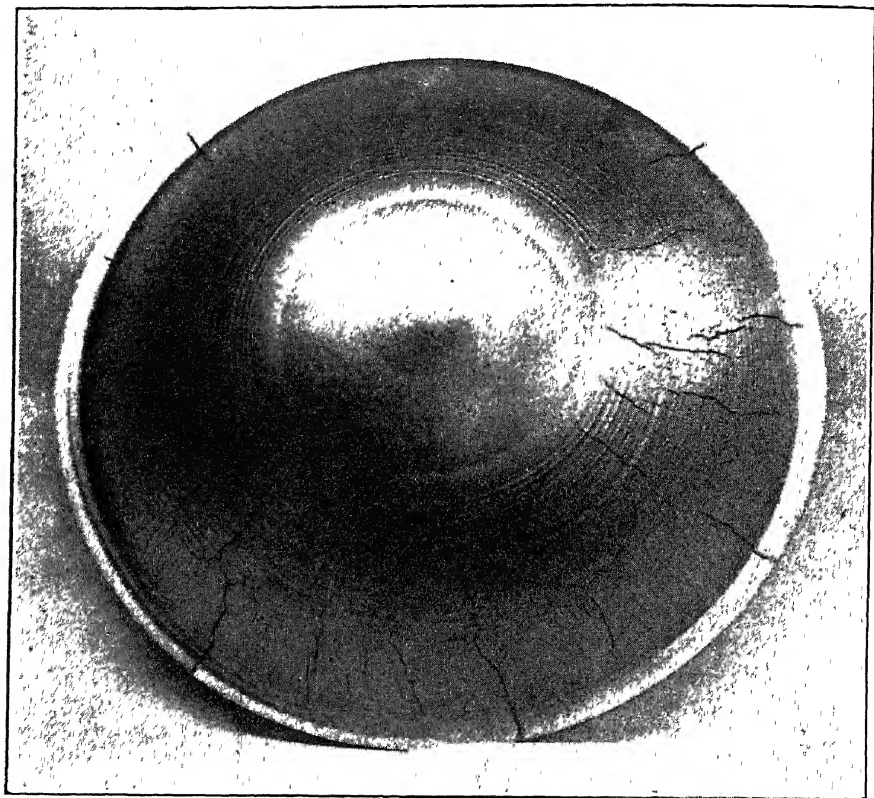
An alloy consisting essentially of copper and nickel, known as *monel metal*, has proved of great value on account of its general resistance to corrosion and to the action of sea-water; and an alloy consisting of 54 per cent. of copper, 45 per cent. of nickel and 1 per cent. of manganese (to increase the tensile strength), is used for ornamental metal work under the name *silveroid*.

**Salts of Copper.**—When exposed to the action of moist air, copper becomes coated with a green-coloured basic copper carbonate called *verdigris*; and the metal readily dissolves in

<sup>1</sup> The term "bronze" is derived from *æs brundusium*. At Brundisium (Brindisi), in Roman times, a hard bronze, used for metal mirrors, was made,

nitric acid with formation of copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ . Copper sulphate, perhaps the best known salt of copper, crystallizes from solution in deep-blue coloured hydrated crystals, having the formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and known popularly as *bluestone*. When added to water in small amount it prevents the growth of algæ.

A mixture of copper sulphate solution and milk of lime,



(Courtesy H. Moore and S. Beckinsale)

FIG. 66.—Season cracking of brass.

$\text{Ca}(\text{OH})_2$ , is largely used—under the name of *Bordeaux mixture*—for spraying fruit trees and bushes, especially vines, to protect them against insect and fungoid pests. About 75 per cent. of the world's production of copper sulphate is used for this purpose.

**Nickel.**—In the seventeenth century, German copper miners, encountering a mineral which appeared to be a copper ore but

from which they could extract no copper, gave to it the name of *Kupfernickel*.<sup>1</sup> From this ore, the Swedish chemist and mineralogist, A. F. CRONSTEDT (1722–1765)—who introduced the valuable analytical technique known as “blowpipe analysis” into chemistry—was able, in 1754, to obtain a metal to which he gave the name nickel. Although first isolated in the middle of the eighteenth century, however, this metal has been found in certain ancient Chinese alloys.

Nickel ores occur mainly at Sudbury,<sup>2</sup> in Ontario, and the metal which is extracted from them is purified by a process invented by the English industrial chemist, LUDWIG MOND (1839–1909), and known as the Mond process. This process is based on the fact that when carbon monoxide is passed over nickel at a temperature below 100° C., combination takes place and a volatile liquid, known as nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , is obtained. On heating the vapour of this compound, decomposition takes place; pure nickel is deposited and carbon monoxide is regenerated, and can be used for the purification of a further quantity of the metal. When in a coherent form, nickel is a hard, white, lustrous metal, highly resistant to the action of the atmosphere. For this reason it is largely used for protecting iron or steel from rust, the metal being deposited by electrolysis (nickel plating). Before being plated with nickel, iron or steel is generally plated with copper.

Besides being used for plating purposes—for which purpose it is being rapidly displaced by chromium—nickel is widely employed as a constituent of many important alloys. Besides those to which reference has already been made, one may mention *nichrome*, an alloy of nickel and chromium with about 23 per cent. of nickel, which is widely used as resistance wire in electrical heaters, and nickel currency alloy, an alloy of nickel and copper containing about 25 per cent. of nickel.

**Cobalt** is a metal similar to and generally found associated with nickel. The name, which is derived from the German *Kobold*, meaning a hobgoblin, was applied by the German miners to certain “false ores” from which copper could not be obtained. The name was, at a later time, applied to the minerals which were found to colour glass blue, and was then transferred to the metallic constituent of the minerals, first isolated in the eighteenth century.

<sup>1</sup> German, Kupfer=copper, and Nickel=a refractory person.

<sup>2</sup> These nickel ore deposits, from which 90 per cent. of the world's supply of nickel is obtained, were discovered only in 1883, when the Canadian Pacific Railway line was being laid through the region lying to the north of Lake Huron. The invention of nickel steel led to the exploitation of the deposits.

So far, few uses have been found for cobalt. Its oxides give a fine blue colour to glass, and it is used in the preparation of certain blue pigments, *e.g.* smalt, obtained by fusing silica with a small amount of cobalt oxide.

**Mercury.**—This heavy, liquid, lustrous metal, the well-known properties of which lend to it a peculiar fascination, was probably first mentioned in literature by Aristotle, who called it *ἀργυρος χυτός* (*argyros chytos*), or liquid silver. A very restricted knowledge of it, however, may have existed at a much earlier period. In later Greek and Roman times, the metal became well known and received the names *hydrargyrum*<sup>1</sup> and *argentum vivum*, that is, living silver or *quicksilver*. By the Arabian alchemists, as we have learned, mercury was regarded as representing the properties of fusibility, malleability and lustre inherent in metals.

Mercury is extracted from the naturally-occurring compound, *mercuric sulphide*, ( $\text{HgS}$ ), or *cinnabar*,<sup>2</sup> a substance which, when ground, yields a powder of a bright red colour. When this substance is strongly heated in a current of air, the sulphur combines with the oxygen to form sulphur dioxide, and the mercury which is liberated is vaporised. By condensing the vapour in cold chambers, the liquid metal is obtained.

Since mercury has a low specific heat, boils at a fairly high temperature ( $360^{\circ}\text{C.}$ ), freezes at a low temperature ( $-39^{\circ}\text{C.}$ ), and does not wet glass, it finds an important application in the construction of thermometers. On account of its high density—it is 13.96 times heavier than an equal volume of water—it was used in the seventeenth century by EVANGELISTA TORRICELLI (1608–1647) for the construction of a barometer.

A number of metals dissolve in or form homogeneous mixtures with mercury. The alloys so obtained are known as *amalgams*, a term first introduced by THOMAS AQUINAS (1227–1274).

Mercury forms two classes of salts, known as mercurous and mercuric salts. The most important of these are *mercurous chloride*,  $\text{Hg}_2\text{Cl}_2$ , or *calomel*<sup>3</sup> (so called from the black colour which this substance gives with ammonia), and *mercuric chloride*,  $\text{HgCl}_2$ , or *corrosive sublimate*. The former compound is sparingly

<sup>1</sup> A Latin form of the Greek name *ὕδραργυρος* (*hydrargyros*), from *ὕδωρ* (*hydōr*), water, and *ἀργυρος* (*argyros*), silver.

<sup>2</sup> Derived from the Greek *κιννάβαρις* (*kinnabaris*). It was used as a pigment (vermilion) and cosmetic, and was frequently confused with red lead or minium. Since the term *kinnabaris* may be derived, so the author is informed, from the ancient Sumerian words, *ku* (silver) and *babbaru* (shining or glistening), it seems not unlikely that the metal was known at a much earlier period than is generally supposed.

<sup>3</sup> From the Greek *καλός* (*kalos*), beautiful, and *μέλας* (*melas*), black,

soluble in water and is used in medicine ; the latter compound is moderately soluble and very poisonous. The solution may be used as a germicide.

**Tin** is one of the metals which were known in ancient times, its alloy with copper, namely bronze, being the earliest alloy of which we have knowledge. Although bronze may have been known before the metal tin had been isolated, it is probable that the Babylonians were familiar with the metal about 2800 B.C. ; and as early as 1000 B.C. the great traders of antiquity, the Phœnicians, obtained this metal from the tin mines of Cornwall, where it was found in the form of its oxide,  $\text{SnO}_2$ , known as *tinestone* or *cassiterite*. To this fact is due the old name of Cassiterides or Tin Islands applied to Britain. For a long time the whereabouts of the Cassiterides remained known only to the Phœnicians, and provoked much anxious curiosity on the part of the Romans. So highly, however, was the secret prized that it is recounted that Phœnician sailors on being followed by a Roman ship while on their way to Cornwall ran their ship ashore rather than betray the position of the valuable tin mines.

Now the glory of the Cornish tin mines has departed. More important deposits have in modern times been found in other parts of the world, chief amongst these being the deposits at Perak and Selangor (Malay States), in Siam, and in the islands of Banca and Billiton in the Dutch Indies. Little, if any, tin is now mined in Cornwall.

Tin is a metal of manifold uses. Its resistance to atmospheric attack has led to its use for coating iron and steel as a protection against rusting. Tin-plate, used for making containers or "tins" for biscuits, preserved foods, etc., is made by dipping steel sheets in molten tin. The malleability of the metal, owing to which it may be rolled out into thin leaves or foil, has also led to its use as a wrapping for chocolate and other materials. So-called *silver paper* is not silver at all, but the much less valuable metal tin.

In association with other metals tin forms part of a number of alloys. Thus we have *bronze* (copper and tin) ; *Britannia metal* and the *Babbitt metals* (tin, antimony and copper), used for bearings of engines ; *pewter* and *solder* (tin and lead).

**White Tin and Grey Tin.**—It has been shown by ERNST COHEN, Professor of Physical Chemistry in the University of Utrecht, that except during the warm summer months, ordinary lustrous tin, or *white tin*, is not in a really stable condition, and that at all temperatures below  $13^\circ \text{C.}$ , it is liable to undergo

change and pass into a less dense form known as *grey tin*. At very low temperatures, and even during severe winters in Continental countries, the change may occur with considerable



(Courtesy Prof. E. Cohen )

Medal showing tin plague.

rapidity. Generally, the conversion of white to grey tin takes place in spots or patches, and owing to the lower density of grey tin, wart-like, powdery growths are formed, the appearance of



which on the surface of the bright metal has earned for the transformation the name of *tin plague*. This "plague," moreover, is contagious, for the conversion of white tin to grey tin is stimulated and accelerated by contact with the latter. All articles of tin—organ pipes, medals, pewter pots, etc.—are liable to suffer from tin plague, and the results may sometimes be disastrous.

**Zinc** occurs in many countries mainly in the form of its sulphide,  $\text{ZnS}$ , known as zinc blende. Some of the most important deposits are found in the United States and at Broken Hill, Australia. The zinc is generally associated with other metals in the ore, so that the ore has first to be subjected to a process whereby the zinc is concentrated. The zinc concentrate is then treated for the extraction of the metal, which in the crude state is known as spelter.

Zinc is a bluish-white metal, the main uses of which are for the production of brass and for galvanising iron. It is also largely used in the construction of the Leclanché and dry cells. Oxide of zinc is used in surgical dusting powders and ointments, and as a pigment under the name of *zinc white*; and a mixture of zinc sulphide and barium sulphate is also employed as a pigment under the name of *lithopone*.

Although brass, an alloy of copper and zinc, was known at an early time, it was not till the sixteenth century that the individuality of the metal was recognised. The name, zinc, is first found in the writings of Paracelsus, who describes the metal as "a quite unusual metal, remarkably rarer than the others."

**Lead** is obtained mainly from the sulphide, *galena*,  $\text{PbS}$ . It is a heavy metal which has been known and used from the earliest times, and which also finds wide application at the present day. Owing to its resistance to atmospheric attack and to the action of acids, this metal is employed for roofing purposes, for sulphuric acid plant, for lining vats in which chemical processes are carried out, etc. It also finds a very widespread use in the manufacture of storage batteries. Lead is so plastic that it can be squirted, under pressure, through dies into the form of rods and pipes, and lead pipes have been used from very early times for the conveyance of water. Water containing carbon dioxide in solution attacks lead fairly readily, but this action is checked by the presence of carbonates and sulphates of calcium and magnesium. Since these salts are present in what is called "hard" water (p. 226), it follows that hard water attacks lead to a much less extent than distilled or than a soft moorland water. Owing to the fact that lead in solution is poisonous,

the resistance of this metal to the action of water is of great importance in connection with the use of lead pipes for the conveyance of drinking water. Where the water of a town's supply is very soft, it may be necessary to "harden" it somewhat by the introduction of small quantities of lime.

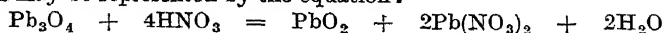
Lead hardened by the addition of a small amount of arsenic is used in the manufacture of shot, and lead hardened by the addition of antimony finds use as type metal. Alloys of lead, tin and bismuth, or lead, tin, bismuth and cadmium, are used as *fusible metals*, some of which melt considerably below the boiling-point of water. Some of these low-melting alloys find application in automatic sprinklers, so that when the heat of a fire melts the alloy, water escapes.

**Oxides of Lead.**—Although lead is not readily attacked by oxygen at the ordinary temperature, it rapidly unites with this element on being heated, and an oxide, lead monoxide ( $\text{PbO}$ ), or *litharge*—an oxide known to the ancients under various names—is formed. On heating this oxide in air to a dull red heat, a higher oxide, known as *red lead*,  $\text{Pb}_3\text{O}_4$ , is obtained as a beautiful, scarlet, crystalline powder, which is extensively used in the production of "crystal" glass, and as a plumber's cement. This oxide, which was, however, not always clearly distinguished from another well-known compound, cinnabar (sulphide of mercury) or vermilion, was called by Pliny, *minium*, a name which the oxide still retains. In the opening centuries of the Christian era, as well as during the Middle Ages, minium was very widely used as a pigment by means of which the early writers and mediæval monks adorned their manuscripts.<sup>1</sup> It was observed by Priestley that when minium is treated with nitric acid, the colour changes, owing to the partial decomposition of minium and the formation of the puce-coloured lead dioxide,  $\text{PbO}_2$ .<sup>2</sup> This oxide, as has been pointed out, forms the material of the positive plate of the lead storage cell.

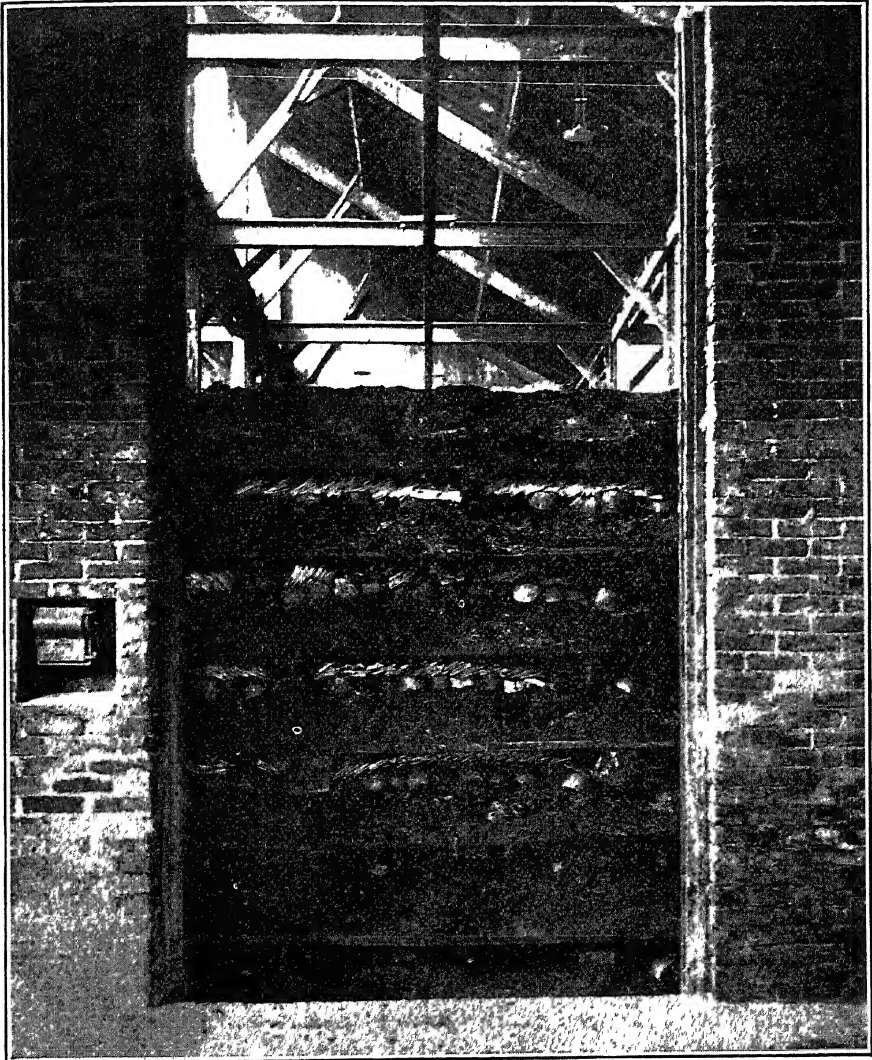
**White Lead.**—As early as the time of THEOPHRASTUS (373–287 B.C.) it was well known that when lead is exposed to the action of the vapour of vinegar (acetic acid) and air, the lead is converted into a white substance—*cerussa*, it was called at a later time by Pliny—and GEBER describes the preparation of this substance "by placing lead above the vapour of vinegar." This white substance, which is now known to be basic lead carbonate,  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , is still prepared in much the

<sup>1</sup> From this use of the pigment is derived the word miniature.

<sup>2</sup> This may be represented by the equation:



same way as two thousand years ago, and forms the pigment *white lead*. Lead plates are supported in earthenware pots, on the bottom of which is a layer of acetic acid. The pots are placed close together, hundreds of them, on a layer of spent and



(Courtesy Etablissements Expert Besançon.  
Manufacture of white lead.

In the picture are shown the tiers of pots embedded in tanner's bark, and the strips of lead placed across the mouths of the pots.

fermenting tanner's bark spread on the floor of the building. The first tier of pots is covered by wooden boards on which a layer of tanner's bark and a second tier of pots are placed; and so on, tier above tier of pots, standing on fermenting tanner's bark and containing plates of lead and acetic acid. As the bark ferments, heat is liberated and carbon dioxide is evolved. The acetic acid is vaporised, and in the presence of atmospheric oxygen attacks the lead plate so as to form a basic lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, \text{Pb}(\text{OH})_2$ . By the action of carbon dioxide, produced by the fermentation of the bark, the basic lead acetate is converted into basic lead carbonate, or white lead: In twelve or thirteen weeks, the whole of the metal is converted into white lead.

When exposed to air containing sulphuretted hydrogen ( $\text{H}_2\text{S}$ ), white lead becomes dark, owing to the formation of black lead sulphide.

**Tungsten**, a metal which, as has been pointed out, finds a most important application in the manufacture of high-speed tool steel, is obtained from the mineral wolfram, a tungstate of iron and manganese. As the metal fuses only at a very high temperature, filaments of tungsten are now universally used in electric incandescent lamps.

Alloys of tungsten, carbon and cobalt, called *carbology* and *widia* (German, *wie Diamant*), can, on account of their diamond-like hardness, be used for metal-cutting tools.

#### NON-FERROUS METALS PRODUCED BY ELECTROLYSIS

**The Alkali Metals.**—Until the year 1807, the alkalis caustic potash and caustic soda were regarded by chemists as elements. In this year, however, HUMPHRY DAVY, at the Royal Institution, London, decided to try whether a decomposition of these substances might not be brought about with the help of the voltaic cells, the invention of which some years previously had created such a sensation in scientific circles. Having constructed a battery of 150 cells, Davy placed a piece of potash on a platinum plate which was connected with the negative pole of the electric battery; and as the dry potash does not conduct the electric current, Davy allowed it to become moist through taking up water vapour from the air. A wire, connected with the positive pole of his battery, was then placed on the top of the moist potash. "Under these circumstances," to quote Davy's own words, "a vivid action was soon observed to take place. The potash began to fuse at both its points of electrification. There

was a violent effervescence at the upper surface; at the lower, or negative, surface, there was no liberation of electric fluid; but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces." Thereby proof was given of the compound nature of potash and a new element—a metal of most unusual properties—was added as an enrichment of scientific knowledge. The discovery aroused great interest, and as his brother relates: "Davy's delight when he saw the minute shining globules burst through the crust of potash and take fire as they reached the air, was so great that he could not contain his joy; he actually bounded about the room in ecstatic delight." Soon after, Davy succeeded also in isolating the metals, sodium, calcium, strontium, barium and magnesium.

**Sodium and Potassium**, two metals of similar character, are at the present day produced by a method essentially the same as that employed by Davy, namely, by the electrolysis of fused caustic soda ( $\text{NaOH}$ ) and fused caustic potash ( $\text{KOH}$ ). These two metals, unfamiliar doubtless to most people, are silvery-white in colour, and very lustrous. When exposed to the air, however, they tarnish immediately, owing to the readiness with which they react with the moisture in the air. They are soft, and of a cheese-like consistency, so that they can be readily cut with a knife. When brought into contact with water, they decompose it with great vigour, with production of hydrogen and formation of caustic soda and caustic potash. Such, in fact, is the vigour of the reaction that the hydrogen which is liberated may become ignited and burn, with a yellow flame in the case of sodium, and a violet flame in the case of potassium. These metals find no application in ordinary life, but are used in considerable quantities in chemical manufactures.

Sodium and potassium are the most important members of a natural family of univalent metals, all of which give rise to hydroxides which are strong alkalis. They are therefore spoken of as the *alkali metals*.

**Aluminium.**—Of the different substances produced with the aid of electricity, the best known and most important is the metal aluminium, at first named aluminum, and still so called in America. It is the most abundant of all the metallic elements in the world, but it occurs naturally only in combination with other elements. Although the sulphate of aluminium, called in

Latin *alumen*, was known to and used as a mordant by the dyers of Egypt and the East before the beginning of the Christian era, and although *potash alum*, the double sulphate of potassium and aluminium,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , was manufactured in Europe as early as the fifteenth century, it was not till 1827 that the metal was first definitely isolated, in the form of a powder, by the German chemist FRIEDRICH WÖHLER (1800–1882). So difficult is it to extract the metal from its compounds by purely chemical methods, that it was not till 1845 that the metal was obtained in a compact form, and it was for long both rare and very costly. In 1886, however, C. M. HALL, a graduate student at Oberlin College, Ohio, and soon after him the French electro-chemist, PAUL L. V. HÉROULT, showed that the metal could be isolated by the electrolysis of a solution of purified bauxite<sup>1</sup> or oxide of aluminium in molten cryolite (a naturally occurring compound,  $\text{Na}_3\text{AlF}_6$ , obtained from Greenland); and the entire world's production of the metal is now obtained by this means. For the electrolysis, an iron bath, lined with graphite, is used and forms the cathode, while large carbon rods dipping into the molten mixture form the anode. As the current of electricity passes through the molten mass, aluminium separates out at the cathode and collects in the liquid form at the bottom of the bath, whence it can be run off from time to time. At the anode, the oxygen which is liberated combines with the carbon electrode, producing the poisonous gas carbon monoxide, which may either escape as such or burn to form carbon dioxide.

Aluminium now occupies a permanent and ever-growing place in our modern life. Not only is the metal used for cooking utensils, but it is being employed more and more in various industries. With the development of the motor car, aluminium, on account of its lightness, finds ever-extending application, and it is essential for the construction of air-craft. It has, moreover, taken to some extent the place of copper for the transmission of electrical energy. The applications of aluminium, further, have been greatly extended owing to the discovery that some of the defects which militated against a more widespread use of the metal—its low tensile strength and softness, for example—can be, to a large extent, removed by admixture with other metals or by subjecting it to suitable heat treatment. Some of the alloys which have thus been obtained possess properties of great value. With copper (about 90 per cent.), aluminium yields a *bronze*, *aluminium bronze*, of great hardness and high tensile

<sup>1</sup> So called because deposits of this mineral were first found near Les Baux, in Southern France.

strength, which is practically not corrodible by sea-water; and when added to brass, aluminium greatly increases the tenacity of that alloy. With the metal magnesium, aluminium forms a valuable alloy called *magnalium* (containing from 1 to 2 per cent. of magnesium), which is even lighter than aluminium itself and is equal to brass in strength; and the construction of airships has been revolutionised by the discovery of the alloy *duralumin*, an alloy of aluminium with copper (4 per cent.), magnesium (0.5 per cent.) and manganese (0.5 per cent.) This alloy, while having a tensile strength equal to or greater than steel, has only one-third of its weight.

It has already (p. 171) been pointed out that aluminium readily combines with the oxygen of the air, if the protective film of oxide is constantly removed. The great affinity of aluminium for oxygen which is thereby indicated, enables the metal to combine with great vigour not only with elementary oxygen, but also with the oxygen contained in compounds. Thus, for example, in the so-called "thermit process," oxide of iron is mixed with powdered aluminium, and the mass strongly heated at one point by means of a special ignition mixture. The aluminium combines with the oxygen of the oxide of iron, and so much heat is thereby generated, that the combustion rapidly spreads throughout the whole mass. Oxide of aluminium is formed, and the metallic iron which is set free is fused. This process is applied to the welding of steel rails and to the repair *in situ* of broken castings, shafting, etc. For this purpose, the molten iron which is produced in the reaction and which has been raised to a temperature of nearly  $3000^{\circ}\text{C}$ ., is run into a mould formed round the ends of the fractured metal. The metal is thus raised to such a high temperature that the broken ends can be welded by pressure, or the fracture may be filled with fresh iron and a solid joint effected.

By means of aluminium, oxides of other metals can be reduced, and by this means chromium, manganese and titanium, which formerly could be extracted only with difficulty, can now be obtained economically and with ease.

**Artificial Rubies and Sapphires.**—The high temperature produced by means of the oxy-hydrogen blowpipe flame (p. 223) has found an interesting and important application in the manufacture of artificial rubies and sapphires. These gems consist essentially of oxide of aluminium (alumina),  $\text{Al}_2\text{O}_3$ , a substance which occurs naturally as corundum, and, in an impure state, as emery. It is a very refractory substance, but it can be melted in the oxy-hydrogen blowpipe flame. When a mixture of 97.5 per

cent. of alumina and 2.5 per cent. of oxide of chromium is heated in the blowpipe flame, it is fused, and, on cooling, solidifies in the crystalline form of the ruby. It is a ruby, identical in chemical and physical properties with the natural gem; and it differs from the latter solely in minute irregularities of internal structure detectible only by the eye of the expert. In the manner described artificial rubies weighing as much as eighty carats, or over half an ounce avoirdupois, have been obtained. These artificial rubies, on account of their great hardness, are now manufactured in large quantities for use in the bearings of watches and for other purposes.

Sapphires can be obtained in a similar manner by fusing a mixture of alumina and small quantities of the oxides of titanium and iron.

**Magnesium**, the metal to which reference was made above, is obtained by the electrolysis of fused magnesium chloride. It is a grey-coloured metal with a density of only 1.74. First produced commercially in England in 1864, its chief use was for the preparation of "flash-lights" in photography, because, on burning, it emits a light which is photographically very active. The Great War, however, created a greatly increased demand for the metal for use in star shells and other signalling devices.



## CHAPTER XX

### VELOCITY OF REACTIONS AND CATALYSIS

THE overthrow of the phlogiston theory by Lavoisier towards the end of the eighteenth, and the enunciation of the atomic theory by Dalton early in the nineteenth century, marked the beginning of a new era in chemical science, when the activities of chemists were directed in an increasing degree to the preparation and quantitative determination of the composition of new substances and naturally occurring materials, as well also as to the determination of the atomic weights of the elements. Moreover, the study of the compounds of carbon, a branch of science to which the name of Organic Chemistry is applied, began to be developed with an ever-increasing energy; and in this domain, the problems connected with the constitution of the molecule, that is, with the arrangement of the atoms within the molecule, were so important for the proper understanding of the enormous array of substances which chemists were able to prepare, that such questions exercised, and very properly exercised, a powerful fascination over the workers in that branch of chemistry. The quite wonderful results which were thereby obtained not only had their value in the domain of theoretical chemistry, but led to some of the most brilliant achievements of practical chemical science—to the preparation of drugs, dyes, perfumes, and many other materials of the greatest industrial and, one may say, human value—so that one need not hesitate to regard such work as amongst the most important in the whole history of the science. The workers who achieved such splendid successes, regarded chemical reactions entirely or mainly from the material point of view, from the point of view of the substances undergoing change and of the substances produced by the change; but there is clearly another aspect of the subject which demands attention. Just as we have already recognised that substances are carriers of energy, and that a chemical reaction or chemical change is a mode of transforming chemical energy into other forms of energy, so also in modern chemistry one is concerned not merely with the material *products* of chemical change, but

also with the *process* of chemical change itself. Why does a chemical reaction take place, and what are the laws governing the rate at which and the extent to which a chemical reaction proceeds? These are the questions which chemical dynamics, one of the most important branches of modern chemistry, seeks to answer.

Although it is not possible to discuss the subject fully here, the attempt must be made to give some indication of the more general principles in order that one may gain a better appreciation of present-day chemistry and a more intelligent understanding of some of the most recent and economically most important industrial processes, the development and success of which depend on dynamical investigations.

**Chemical Affinity.**—When, in the thirteenth century, the great Dominican monk and Bishop of Regensburg, ALBERTUS MAGNUS, used, in his *de rebus metallicis*, the word “affinitas,” he merely summed up views derived from ancient Greek philosophy and current at that time, that chemical reaction is due to a similarity or kinship between the reacting substances; or, as maintained by Hippocrates, that “like unites only with like.” In the eighteenth century, however, this view was abandoned by BOERHAAVE (1732) and others, who maintained that dissimilar substances show the greatest tendency to combine; and, at the present time, the term affinity or chemical affinity, although still in use, must be regarded not as signifying any natural resemblance or family relationship, but rather as a force, electrical in nature, which acts between different kinds of matter and which, under certain conditions, brings about a chemical action between them. The existence of this force is postulated in order to account for the fact that chemical change or reaction will take place between substances when thereby potential energy can be converted into work.

Affinity, or chemical affinity, it should be noted, does not give an *explanation* of chemical change; it is, rather, a measure of the work done by a system when it undergoes change. It is equivalent to the electromotive force of a voltaic cell (and in the case of reactions between electrolytes this is the best measure of affinity), or the height of fall of water. An *explanation* of chemical change is rather to be found in the electronic constitution of matter, as discussed in Chapter VI.

**Law of Mass Action.**—One of the most important factors in the process of chemical change is the speed with which it takes place, the velocity of the reaction. That there are great differences in the rate at which chemical change takes place is

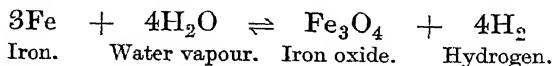
so obvious as almost to render its emphasis unnecessary. The rusting of iron, the oxidation of aluminium, the burning of wood, the explosion of gun-cotton, are chemical changes which take place with markedly different velocities. These great differences in the rate of reaction we shall be inclined to attribute to differences in the chemical affinity, and in doing so we shall be right, but only partly right: for when one studies the process of chemical change more fully, it is found that the rate of a reaction does not depend merely on chemical affinity, but also on a number of other factors the nature of which is not always clearly understood.

Even in the case of one and the same reaction, the velocity of change may be markedly affected by various factors, of which one of the most important is the *concentration* of the reacting substances, that is, the amount of the substances in a given volume. We shall be able to understand this more readily if we fix our attention, for the present, on reactions between gaseous substances. When a substance is in the gaseous state, its molecules are supposed, according to the kinetic theory of matter, to be moving about with great velocity in all directions, and combination or reaction between two substances, A and B, can take place only when molecules of A and B collide or come within each other's sphere of influence. If, then, there are a certain number of molecules of A and of B moving about in a given space, an A molecule will encounter a B molecule a certain number of times per second, and the rate of reaction, therefore, will have a certain value. Suppose that the number of B molecules is now doubled. It is clear that in the same unit of time, an A molecule will now have double the number of chances of encountering a B molecule and of entering into reaction with it, and the rate of reaction will therefore be twice as great as it was originally. Similarly, if the concentration not only of the B molecules but also of the A molecules be doubled, then it is clear that the rate of reaction will again be doubled; that is, the reaction now takes place four times as fast as it would have done with the original concentrations of the two substances. *The speed of a reaction, in short, is proportional to the product of concentrations of the reacting substances*, the concentration being expressed in gram-molecules per litre. This law of the dependence of the speed of a chemical change on the concentrations of the reacting substances is generally known as the **LAW OF MASS ACTION**—it might more correctly be called the law of concentration action—and was enunciated in 1867 by two Norwegian scientists, CATO MAXIMILIAN GULDBERG (1836–

1902), who became Professor of Mathematics in the University of his native town of Christiania (Oslo), and his brother-in-law, PETER WAAGE (1833–1900), who was born at Flekkefjord, in Southern Norway, and in 1862 became Professor of Chemistry in the University of Christiania.

The velocity of chemical change, however, is also very greatly influenced by the *temperature*, a fact to which we have already alluded (p. 169). Although the speed of different reactions is affected in a different degree by temperature, it may be taken as a convenient approximation that the speed of a reaction is doubled by raising the temperature 10° C. A simple calculation will show what the magnitude of this effect may be. Suppose that a reaction requires one second for its completion at 0° C. At 100°, the boiling-point of water, the same change would take place in about one-thousandth of a second; and if the temperature be raised but a little more, say to 200° C., the time required for the change will now be only about one-millionth of a second. On the other hand, a change which would require one second to take place at 200°, would need, at 0°, a period of a million seconds, that is, about eleven and a half days. This influence of temperature is of the greatest importance, and on its recognition may depend the success of an industrial process.

**Reversible Reactions and Equilibrium.**—A further very important result which has followed from the dynamical study of chemical reactions is the recognition of the fact that *chemical changes are reversible*, and that the direction in which reaction between different substances takes place depends not merely on chemical affinity but on the relative concentrations of the different substances. When steam (oxide of hydrogen) is passed over heated iron, oxide of iron and hydrogen are produced. On the other hand, when hydrogen is passed over heated oxide of iron, steam (oxide of hydrogen) and metallic iron are formed. This fact is represented by means of two oppositely directed arrows in place of the symbol of equality in the chemical equation, thus :

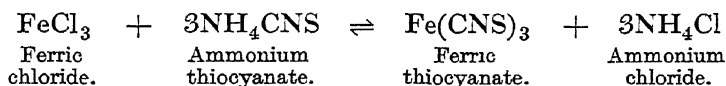


In the former case, the steam is present in large abundance, whereas the hydrogen which is formed is swept away and cannot, therefore, react with the oxide of iron. In the latter case, the hydrogen is present in abundance, while the water vapour is carried away in the stream of gas and so is prevented from reacting with the metallic iron. By altering the relative concentrations of the steam and the hydrogen, therefore, one can

cause reaction to take place in whichever direction one pleases. Suppose, now, that the experiment is arranged in such a way as to prevent the removal of the hydrogen or of the steam, as can be done by heating all four substances together in a closed vessel, then it will be found that both reactions will take place; steam will react with iron, and hydrogen will react with oxide of iron, so that finally a state of balance or *equilibrium* will be produced, at which there will be a certain definite relationship between the concentration of the steam and the concentration of the hydrogen.<sup>1</sup>

The production of a state of equilibrium must not be interpreted as indicating that there is a complete cessation of chemical change, but rather that the velocities of the two opposing reactions have become equal. If, therefore, the concentration, say, of hydrogen is increased, by pumping hydrogen into the reaction vessel, the velocity of reaction between hydrogen and oxide of iron will be increased, and so a further amount of oxide of iron will be reduced to the metallic state, with production also of a further quantity of water vapour.

The fact that a reversible reaction may be made to take place in one direction or the other by altering the concentrations of the reacting substances, can be demonstrated by means of the reactions represented by the equation :



Solutions of ferric chloride and ammonium thiocyanate are prepared which contain about  $\frac{1}{300}$ th of a gram-molecule of the salt (*i.e.* 0.54 gram of ferric chloride and 0.25 gram of ammonium thiocyanate) per litre. When equal volumes of these solutions are mixed, a blood-red coloration is produced, due to the formation of ferric thiocyanate. The liquid is now divided into two parts; to one part is added solid ammonium thiocyanate, and to the other, solid ammonium chloride. In the former case, the colour becomes much deeper, showing that more ferric thiocyanate is formed; the reaction therefore takes place from left to right. In the latter case, the colour becomes paler, showing that the concentration of the ferric thiocyanate is diminished; the reaction therefore takes place from right to left.

<sup>1</sup> The reaction is regarded here as taking place in the gaseous state, and, consequently, the concentration of the iron and of the iron oxide molecules may be regarded as constant, so long as these two substances are present in the solid state. The justification of this is that the concentration depends on the vapour pressure, and this, however small it may be, is constant at a given temperature.

**Theorem of Le Chatelier.**—In the case of any given reversible process, the same state of balance or equilibrium is reached, so long as the temperature is kept constant, the equilibrium condition being, in general, in accordance with the expression :

$$\frac{\text{product of concentrations of reactants}}{\text{product of concentrations of resultants}} = \text{constant.}$$

The *reactants* are the substances on the left side of the chemical equation and the *resultants* the substances on the right. By raising or lowering the temperature the one or the other reaction can be caused to take place to a greater and greater extent, and the direction in which the equilibrium is thereby altered is found to be intimately associated with the heat effects which accompany the chemical change. The law which obtains here can be stated in a simple form, it being borne in mind that if one reaction is accompanied by an evolution of heat, the reverse reaction must be accompanied by an absorption of heat. The law referred to states: *When the temperature is raised, the reaction which takes place with absorption of heat, is favoured; whereas lowering the temperature favours the reaction which takes place with evolution of heat.* Only when no heat effect accompanies chemical change is the equilibrium unaffected by change of temperature. This law is part of a general theorem enunciated in 1884 by HENRI LOUIS LE CHATELIER, Professor of Chemistry in the University of Paris, and known as the **THEOREM OF LE CHATELIER**.

The discovery of the laws of chemical change, and the recognition that, theoretically at least, all reactions are reversible, mark one of the most important advances in our knowledge of chemical processes and of the action of chemical affinity. Some of the consequences which flow from this will be discussed in the sequel.

**Catalysis.**—Although, as has been said, the progress of a chemical reaction and the rate at which a chemical change proceeds, are influenced both by the concentration of the substances and by the temperature, it is found that the velocity of a chemical reaction may also be profoundly affected in another way which, on account of its very great importance both in the laboratory and in the factory, demands a fuller consideration.

In the early decades of last century, a number of phenomena were observed which, although isolated and apparently unconnected, all possessed one common characteristic, namely, that the rate at which a chemical change or process takes place

is increased to a greater or less extent, by the addition of certain substances in minute, sometimes in almost infinitely minute, amount. Owing to such additions, it was found, substances which seemed, under the particular conditions, to be without action on each other, reacted with appreciable, sometimes even with great, readiness. From the magnitude of the result produced, it was evident that the foreign substance could not enter into the reaction in the ordinary way; but, as the Swedish chemist, BERZELIUS, pointed out, the substance which was added appeared to act merely by its presence and by "arousing the slumbering affinities of the substances," and so allowing them to react. How these slumbering affinities were aroused, Berzelius did not hazard a guess, but in order to give a name under which such phenomena could be classed, he introduced, in 1838, the term "catalysis" (a word which signifies a loosening); and a substance which brings about catalysis is called a "catalytic agent" or a "catalyst." For long the phenomenon of catalysis, of which the number of cases observed rapidly increased during the nineteenth century, was regarded by chemists as Gulliver was regarded by the learned men of Brobdingnag, as a *lusus naturæ*; it was relegated to the realm of the mysterious, and chemists became only too prone to think that the label of catalysis was at the same time an explanation of the phenomenon. It was, indeed, only towards the end of last century, and owing to the development of the experimental methods of measuring the rate of chemical change, that the phenomenon of catalysis and the behaviour of catalysts began to form the subject of systematic investigation. This renewed investigation of catalytic phenomena was undertaken mainly under the influence of WILHELM OSTWALD,<sup>1</sup> who emphasised that the most characteristic feature of the phenomenon was the change in the *velocity* of reaction, and insisted that before any explanation of the action could be attempted, it was necessary to investigate quantitatively *how* the velocity of a reaction is altered by the presence of catalysts. Moreover, in order that the field of investigation might be delimited, Ostwald defined a catalyst as "*any substance which without itself appearing in the final products of reaction, alters the velocity with which that reaction takes place*"; that is to say, the catalyst undergoes no change in amount or in chemical composition during the reaction. In the preparation of oxygen, for example, by heating potassium chlorate, the decomposition of this salt is

<sup>1</sup> Wilhelm Friedrich Ostwald was born at Riga in 1853, and from 1887 to 1905 occupied the Chair of Physical Chemistry in the University of Leipzig. In 1909, he was awarded the Nobel Prize in Chemistry.

greatly accelerated by manganese dioxide (p. 152), the whole of which can be recovered at the end of the reaction. Moreover, the reaction velocity may be diminished (negative catalysis) as well as increased (positive catalysis), but the latter behaviour is the commoner and more important.

It is important to bear in mind that one is dealing here merely with the *definition* of a term, not with the explanation of a process, and it is therefore open to any one to define the term otherwise. It is a question merely of suitability and convenience.

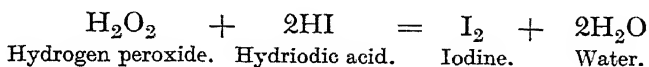
Since, by definition, the catalyst remains unchanged in amount and chemical composition, it cannot give up energy to the reaction, and cannot, therefore, alter the driving force of the reaction. It can increase the speed of a reaction only by diminishing the resistance to chemical change (whatever the nature of the resistance may be); or, as Ostwald has put it, a catalyst acts like a lubricant in the bearings of a machine. The presence of the lubricant enables the machine to run more rapidly, but the lubricant itself is not used up in the process. One must not, however, press the analogy unduly, for although the catalyst may undergo no diminution in amount or permanent change in chemical composition, its physical state may be altered. Compact manganese dioxide, for example, when used as a catalyst for the decomposition of potassium chlorate, may be disintegrated to a powder, and a smooth platinum surface becomes roughened when used as a catalyst for the oxidation of ammonia to nitric acid (p. 373).

**Small Causes and Great Effects.**—As has already been indicated, one of the most striking features of catalysis is the magnitude of the effect produced, compared with the small amount of the substance producing it. An excellent illustration of this is seen in the influence which *moisture* exercises on the rate of combination of gaseous substances. When hydrogen and oxygen, the two gaseous substances by whose combination water is formed, are heated together, they combine, and if the temperature is sufficiently high, say about  $600^{\circ}\text{C.}$ , the combination takes place with explosive violence. But this occurs only when a trace of moisture is present in the gases. If the last traces of moisture are removed from the gases by prolonged contact with phosphorus pentoxide—a substance which, as has been pointed out, combines with the greatest avidity with water—the mixture of hydrogen and oxygen can then be heated even to a temperature of nearly  $1000^{\circ}\text{C.}$ , without explosion occurring. Not only in the case of hydrogen and oxygen, but in the case also of many other gases (*e.g.* carbon monoxide and oxygen),



combination is found to depend on the presence of moisture, of which, however, the merest trace suffices.

In astronomy, one deals with magnitudes so vast as to be beyond the grasp of our minds. In the domain of catalysis, the magnitudes are, in some cases, so small that it becomes almost equally impossible to form a true conception of them. The effect of almost inconceivably small amounts of moisture, such as may still be left in a gas which has been dried by means of concentrated sulphuric acid, has already been indicated; and the influence of minute quantities of other catalysts on the velocity of a reaction may be illustrated by various reactions which take place in solution. Thus the velocity of the reaction:



is more than doubled by the presence of molybdic acid in a concentration of 1 gram-molecule (162 grams of  $\text{H}_2\text{MoO}_4$ ) in 1,000,000 litres; and the accelerating influence can be detected even when the concentration is 1 gram-molecule in 32,000,000 litres. A similar accelerating power is shown by tungstic acid.

A still more striking case of catalytic acceleration is found in the influence of copper on the oxidation of solutions of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) by oxygen so as to form sodium sulphate ( $\text{Na}_2\text{SO}_4$ ). In the absence of catalysts, this reaction takes place only slowly, but the rate of oxidation is enormously increased by the presence of small quantities of the salts of the heavy metals, more especially of copper. Thus, the presence of even 6.36 grams of copper, in the form of copper ions, in 100,000,000 litres<sup>1</sup> (or  $6.38 \times 10^{-8}$  gram in 1 litre), can be readily detected by its catalytic action. Even water which has remained in contact with metallic copper for three-quarters of a minute, contains sufficient copper to show a noticeable effect. An impressive illustration, surely, of the importance of the infinitely small.

In general, catalytic acceleration is proportional to the concentration of the catalyst; but when two catalysts are added to the reaction mixture, the effect is sometimes merely additive and sometimes there is a mutual strengthening or a mutual diminution of the catalytic effect. Sometimes, again, the addition of a substance which itself has no catalytic action, may increase the activity of a catalyst already present. Such a substance is spoken of as a *promoter*. This action is very

<sup>1</sup> About 1 grain in 250,000 cubic feet (1,557,000 imperial gallons) of water.

commonly met with in the case of solid catalysts in heterogeneous systems (see below).

**Autocatalysis.**—Not only may the velocity of a reaction be altered by the addition of a substance which is foreign to the reacting system, but it may also be altered either by one of the substances which are themselves undergoing reaction, or by one of the products of reaction. When pure nitric acid is poured on copper at the ordinary temperature, no immediate reaction is observed. The pure acid acts only very slowly. Gradually, however, the rate of reaction becomes greater and greater because the *nitrous acid*,  $\text{HNO}_2$ , which is produced in the course of the action by the reduction of nitric acid ( $\text{HNO}_3$ ), acts catalytically and accelerates the process.

**Negative Catalysis.**—Not only may the velocity of a reaction be increased by a catalyst, but it may also be decreased. This is the phenomenon of *negative catalysis*. Thus, although moisture accelerates the combination of hydrogen and oxygen, it retards the decomposition of ammonia; and whereas a copper salt greatly accelerates the oxidation of sodium sulphite by oxygen, a tin salt is only about twenty times less effective in *retarding* the oxidation. Further, the oxidation of sodium sulphite by oxygen is greatly retarded by small quantities of various alkaloids. Even a puff of tobacco smoke (containing nicotine) through the solution produces a detectible retardation of the oxidation.

At the present time negative catalysts or inhibitors of chemical change find many important applications. Hydrogen peroxide which, as has been pointed out, somewhat readily undergoes decomposition, can be stabilised by addition of a small amount of phenacetin, and the oxidation process which causes rubber and silk, for example, to “perish,” can be greatly retarded by means of thiourea,  $\text{CS}(\text{NH}_2)_2$ , and other substances.

**Catalysis in Heterogeneous Systems.**—Catalysis may occur not only in homogeneous but also in heterogeneous systems, as when solid substances act as catalysts in gaseous and liquid systems. As early as 1817, Sir HUMPHRY DAVY discovered that when a spiral of platinum wire, slightly heated, was suspended in a vessel containing a little alcohol, the oxidation of the alcohol vapour by the oxygen of the air took place so rapidly at the surface of the platinum wire, that the latter was speedily raised to incandescence, and a “lamp without flame” was thus obtained. Unlimited quantities of alcohol vapour can thus be caused to burn rapidly by the same piece of platinum, and the latter betrays no sign of change in the process. Similarly,

platinum accelerates the combustion of hydrogen, carbon monoxide, ammonia (p. 373), and many other gases; and since the catalytic action can take place only *at the surface* of the catalyst, the effectiveness of the latter will be all the greater the more finely divided it is, or the greater the surface exposed. Thus, if *finely divided platinum*, known as platinum black, be introduced into a mixture of hydrogen and oxygen at the ordinary temperature, the combination of the two gases may be accelerated to such an extent that the platinum becomes red hot, from the heat of combustion, and brings about the explosive combination of the gases. Catalysis which, as in the case just considered, takes place at a surface of contact, is known as *contact catalysis*.

The remarkable behaviour of finely divided platinum to which reference has just been made, greatly impressed, as well it might, the minds of the early observers, and was not long in receiving a practical application. In 1823 it was observed by DOBEREINER that when a jet of hydrogen was allowed to impinge on a piece of spongy platinum exposed to the air, the heat of combustion of the hydrogen raised the platinum to incandescence and the hydrogen became ignited. Dobereiner constructed an apparatus in which hydrogen was produced by the action of sulphuric acid on zinc; and when a tap was opened the gas escaped in a fine jet and impinged on a piece of spongy platinum. In this way fire could be obtained, and, as a matter of fact, this Dobereiner lamp was largely used for that purpose before the days of matches.

Spongy platinum is also used in certain automatic gas lighters which are on the market. These, however, lose their effectiveness after a time owing to the "poisoning" or destruction of the catalytic activity of the platinum by impurities present in the gas.

Although platinum is by no means a universal catalyst for all reactions—no such universal catalyst is known—it has nevertheless been found that platinum acts very generally as a catalytic accelerator of oxidation reactions, or reactions in which gaseous oxygen takes part. Oxide of cerium, which forms a small part of the Welsbach incandescent gas mantle, also acts as a catalyst and accelerates the combustion of the coal gas.

Since, in contact catalysis, the effectiveness of the catalyst depends on the extent of surface exposed, it is found that substances in the state of fine subdivision known as the colloidal state (Chapter XXV) are very effective as catalysts; and the action of colloidal platinum, for example, has received a large amount of study. As in the case of homogeneous catalysis, so

also here, one is impressed by the magnitude of the effect brought about by small quantities of the catalyst. Thus, in the catalytic acceleration of the combination of hydrogen and oxygen by colloidal platinum it was found that 2.5 c.c. of a colloidal platinum solution, containing only 0.17 milligram of the metal, sufficed to bring about the combination of hydrogen and oxygen at the rate of 1.8 c.c. of the mixed gas per minute. This rate, moreover, was maintained over a period of fourteen days, with interruptions at night, and during this time about ten litres of the gas had undergone combination. Even then the activity of the platinum was unimpaired.

Not less remarkable is the catalytic action of colloidal platinum in accelerating the decomposition of hydrogen peroxide, the catalytic activity being detectible even when the colloidal platinum is present only in the amount of 1 gram-atom (195.2 grams) in 70,000,000 litres.

**Enzymes as Catalysts.**—In the action of the inorganic colloidal catalysts, one finds a very interesting model of the action of the organic enzymes in accelerating the complex analytic and synthetic processes which go on in the living organism, and which are concerned in the large class of reactions generally referred to as fermentation processes.

The explanation of the fermentation<sup>1</sup> process—a term at first applied to all changes which are accompanied by effervescence due to the escape of gas—is one which has been accepted by science only during the present century. Prior to 1857, chemists and biologists were divided in their views. Some favoured the physical and chemical explanation put forward by Berzelius, who likened fermentation to the decomposition of hydrogen peroxide under the catalytic action of platinum, while others regarded the process as the direct result of vital activity. The question seemed definitely to be settled when, in 1857, PASTEUR, to whose genius the advance of science in many directions is due, proved conclusively that all fermentative changes are associated with living organisms. The vitalistic explanation, therefore, summed up in the well-known phrase, “No fermentation without life,” became generally accepted. For a considerable time the view was held that the fermentation processes are the result of the direct action of the living organism on the fermentable material; but doubt arose when cases began to accumulate of changes brought about by substances, *e.g.* diastase and pepsin, which are the product, certainly, of life but are not themselves living. The matter was put beyond dispute when, in 1897, the German

<sup>1</sup> From the Latin *fervere*, to boil.

chemist, EDUARD BUCHNER, showed that, in the production of alcohol from sugar, the fermentation is brought about not by the direct action of the living organism, but by a substance, which he called *zymase*, produced by and contained in the cell of the yeast. It is now generally accepted, therefore, that fermentation changes are produced by substances which although produced by living organisms are not themselves living; and to these substances the name *enzyme*,<sup>1</sup> suggested by the German physiologist, W. KÜHNE, in 1878, is applied.

The enzymes, then, are catalysts which are produced in the living cells of plants and animals—even in the humble cells of the micro-organisms, yeasts, bacteria and moulds—and through the presence of which the varied changes of an ever-changing Nature take place. Putrefaction and decay; the souring and curdling of milk; the production of the dye-stuff indigo from the compound indican contained in the woad; the “puering” of hides and the curing of tobacco; the development of the pungent flavour of mustard and the production of benzaldehyde or oil of bitter almonds from the amygdalin contained in the almond seed; all these and many other processes by which complex organic material is broken down into simpler substances, are brought about under the catalytic influence of appropriate enzymes produced in the cells of living organisms.

Like the inorganic catalysts, the organic catalysts or enzymes are specific in their action. The enzyme maltase, for example, accelerates the conversion (hydrolysis) of maltose (malt sugar) to glucose but is without action on cane sugar (sucrose); and invertase, similarly, accelerates the hydrolysis of sucrose but not of maltose. For the conversion of starch to glucose, also, a special enzyme, diastase, is produced in the sprouting barley corn; and the hydrolysis of proteins is accelerated by the pepsin in the gastric juice and the trypsin secreted by the pancreas. And so, in the busy laboratory of the living organism, the numerous and varied processes of analysis and synthesis, oxidation and reduction, are carried out under the influence of appropriate enzymes or catalysts which regulate the rate at which the reactions take place to that required for the healthy functioning of the organism as a whole. Interference with the production or action of these catalysts results in disturbances of the life processes, disease and, it may be, death.

Not only do the enzymes play an indispensable rôle in the economy of Nature, but they also play an essential part in many of the most important industrial processes, such as that which

<sup>1</sup> From the Greek *ἐν ζύμῃ* (*en zymē*), in yeast.

has been carried on from an early period in man's history, the production of alcohol by the fermentation of sugar. The recent study of chemical processes brought about under the influence of enzymes has led to a great increase in the industrial utilisation of enzyme-producing micro-organisms.

**The "Poisoning" of Catalysts.**—Reference has been made to the occurrence of negative catalysis, and the phenomenon can, in many cases at least, be regarded as due to the destruction or repression of the catalytic activity of a catalyst by another substance. This inactivation has long been known and is met with among the inorganic as well as among the organic catalysts; and in analogy with the action of certain substances on the catalytic activity of cell enzymes, the term "poison" is very generally applied to substances which bring about a repression of positive catalysis. The poisoning of colloidal platinum as a catalyst for the decomposition of hydrogen peroxide has been fully investigated, and it has been found, for example, that the catalytic activity of the platinum can be noticeably reduced by hydrocyanic acid (HCN) or "prussic acid," even when the concentration of the latter is only 1 gram-molecule (27 grams) in 20,000,000 litres.

The possibility that a catalyst may be "poisoned" by even small amounts of impurity present in a reaction mixture or formed in the course of a reaction, is of the greatest theoretical and practical importance, and must constantly be borne in mind.

**Mechanism of Catalysis.**—Although a very wide range of catalytic phenomena has been subjected to most careful investigation, the mechanism of catalysis cannot yet be said to have been fully and adequately explained. In a considerable number of cases, cases of so-called transfer catalysis, the most plausible and acceptable explanation is to be found in the assumption that a slightly stable compound is formed between the catalyst and one of the reacting substances, and that this compound then undergoes reaction with the other reactant with formation of the reaction product and re-generation of the catalyst. Or, in other words, if A and B are the reactants and C is the catalyst, formation of the reaction product AB would take place in the two stages:  $A + C \rightarrow AC$  and  $AC + B \rightarrow AB + C$ . In these cases, the one reacting substance is carried or transferred, as it were, to the other reacting substance.

Although there is much experimental evidence in support of such an explanation, there still remains unanswered the question: Why does a reaction take place more rapidly by indirect

stages, that is, by alternate formation and decomposition of an intermediate compound, than directly in one simple process? This question cannot yet be adequately answered.

In the case of contact catalysis, it seems probable that catalytic acceleration is brought about by an *adsorption* or condensation of the reacting substances on the surface of the catalyst, whereby the effective concentration of the reacting substances is increased. To explain this adsorption effect, the view has been advanced, more especially by H. S. TAYLOR, of Princeton University, that at the surface of the catalytically active solid the crystalline structure is not compact but rather dendritic (p. 127) in character, as indicated in Fig. 67; and that the atoms forming the dendrites have therefore free valencies

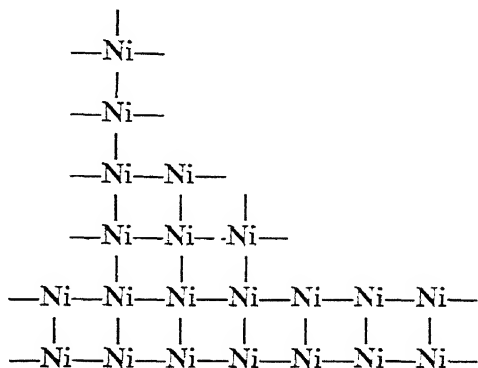


FIG. 67.—Catalytic surface of nickel.

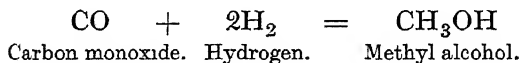
by which they can unite, in a slightly stable manner, with the substances undergoing reaction.

**Catalysis in Industry.**—In the manufacturing industries, it may truly be said that time is money; and to produce an article of manufacture at a more rapid rate is the same as saving time. And this is just what a catalyst enables one to do. During the present century, more especially, the value of catalysts in industry has become increasingly recognised, and the systematic search for a suitable and effective catalyst for a given reaction is a well-established part of chemical investigation. As a result of this, reactions which by reason of their sluggishness are industrially useless, have been developed into great and important industries through the acceleration of the reaction by suitable catalysts. In this way there have developed the great industries of synthetic ammonia and nitric acid (p. 371), of contact sulphuric acid (p. 345), of the hydrogenation of oils

(p. 436), etc., which will be discussed later. The twentieth century, in fact, might be called the catalytic age in chemical manufacture.

Mention has already been made of the fact that the action of catalysts is largely specific, and by a proper choice of catalyst and regulation of the conditions of reaction, it is found that the same substances may be made to react in various ways. No better illustration of these statements, perhaps, could be obtained than what is offered by the numerous products which can be obtained from the mixture of carbon monoxide and hydrogen known as water gas, which is produced, it may be recalled, by the passage of steam over red-hot coke.

Until about 1925, methyl alcohol (methanol) or "wood spirit," which is used in large quantity in the manufacture of dyes, perfumes, etc., was produced in the United States, Canada, Germany and Sweden, by the distillation of wood. This great industry, however, received, in 1924, a serious blow when, mainly through the researches of French and German chemists, it was shown that methyl alcohol can be readily produced by passing a mixture of carbon monoxide and hydrogen over a suitable catalyst (zinc oxide or a mixture of zinc oxide and chromium oxide) under regulated conditions of temperature and pressure. In presence of the catalyst, the inconceivably sluggish reaction represented by the equation:



takes place with such readiness that the process becomes economically successful. The industrial production of methyl alcohol by this process is now well established not only in Germany, the home of the process, but also in England, France, Italy and America.

From the mixture of carbon monoxide and hydrogen, moreover, by the use of different catalysts and by suitable variation of the conditions of temperature and pressure, many other substances may be obtained, such as butyl alcohol—a valuable solvent for nitro-cellulose lacquers—and mixtures of hydrocarbons suitable for motor fuel. These processes, however, are at present only in course of development.

At the present time very large amounts of water gas are employed as a source of hydrogen for the production of ammonia, and although, as we have seen, the hydrogen may be freed from the carbon monoxide by liquefaction, a catalytic method is mainly employed. Thus, when water gas is heated with steam



at a temperature of about  $500^{\circ}\text{C.}$ , in presence of a catalyst which consists essentially of iron oxide, the carbon monoxide reacts with the steam and gives rise to carbon dioxide and hydrogen, the carbon dioxide being thereafter removed by dissolving in water under pressure.

## CHAPTER XXI

### SULPHUR AND SULPHURIC ACID

#### SULPHUR

Just as in the case of the halogens—fluorine, chlorine, bromine and iodine—and of the alkali metals—lithium, sodium, potassium, rubidium and caesium—we meet with groups of elements, the members of which exhibit certain “family resemblances,” so in the case of the elements oxygen, sulphur, selenium and tellurium, another such group is found. Although very different in outward appearances, these elements exhibit their family relationship more especially in the similarity of composition of the compounds which they form. Oxygen, for example, forms with hydrogen a compound, water, the composition of which is represented by the formula  $H_2O$ ; and sulphur, similarly, forms a compound, hydrogen sulphide or sulphuretted hydrogen, the composition of which is represented by the formula  $H_2S$ . With carbon, also, oxygen and sulphur form compounds of analogous composition, namely, carbon dioxide,  $CO_2$ , and carbon disulphide,  $CS_2$ . Moreover, sulphur combines readily with many metals to form sulphides which are analogous to the oxides of the metals. Thus, when sulphur and iron are heated together combination takes place with formation of iron sulphide,  $FeS$ , analogous to the oxide,  $FeO$ ; and sulphur also combines vigorously with copper to form the sulphide,  $CuS$ . This reaction, whereby the metallic properties of the copper are destroyed, was doubtless known some thousands of years ago, and to it presumably we owe the name sulphur.<sup>1</sup> Many other compounds are known in which the place of an oxygen atom is taken by an atom of sulphur. It is true that the family resemblances between the members of the oxygen-sulphur group are by no means so marked or clearly defined as in the case of the halogen elements or of the alkali metals; nevertheless, these family relationships are, from the chemical point of view, of much importance and

<sup>1</sup> According to some authorities, the name sulphur is derived, through the Latin, from the Sanscrit word *sulvari*, which means “hostile to copper.”

have proved very helpful in stimulating and guiding the investigations of chemists.

A knowledge of sulphur doubtless extends back to a very early period in the history of civilisation, for this element is found in the free state, very widespread, in regions of past and present volcanic activity. As early, at least, as the time of Homer, about a thousand years before the Christian era, the medicinal and fumigating properties of sulphur were being applied, and by the first century A.D., the mining and refining of sulphur were important industries in the islands of the Mediterranean. The finest sulphur, according to Pliny, came from the island of Melos (Milo). The combustibility of sulphur led in Europe to the name of *brimstone* or *brennestone* (*i.e.* burning stone); and the Arabian and later alchemists in putting forward the view that metals are composed of sulphur and mercury, had this property of combustibility rather than the substance itself in mind.

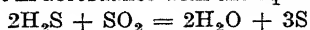
Although one can no longer regard sulphur as possessing the manifold virtues attributed to it in early times<sup>1</sup> and during the Middle Ages, it is nevertheless a substance of great economic importance at the present day. Thus, large amounts are used for combating the attacks of fungi and of insect pests on vines and hops, and it is also used in the vulcanising of rubber and the manufacture of black gunpowder. In the main, however, sulphur finds its chief use in the manufacture of sulphuric acid and of calcium sulphite, which is used in the production of wood pulp.

Although sulphur has been formed in the past, and is being formed also at the present day, by reaction between hydrogen sulphide and sulphur dioxide,<sup>2</sup> which are present in the gases emitted by volcanoes, it is probable that the chief workable deposits of sulphur have been produced by a decomposition of calcium sulphate (gypsum and anhydrite).

**Production of Sulphur.**—Until about 1903, almost the whole world-supply of sulphur was obtained from the sulphur deposits which are found, over an extensive area, in the provinces of Caltanissetta and Girgenti, in Sicily. In that year, it is stated, 37,500 operatives were employed in the sulphur mines, many of whom were little more than children. These acted as porters (*carusi*) and carried the ore from the working face to the surface. Bearing a load of 30–50 kilograms, they “had to make twenty-

<sup>1</sup> According to Pliny, “sulphur is of such remarkable virtue, that if it is thrown on the fire it will detect, by the smell, whether or not a person is subject to epilepsy.”

<sup>2</sup> These two gases react in accordance with the equation .



five or thirty journeys a day, half naked, bathed in sweat, covered with dust, with a closed lamp affixed to the top of the head, accompanying their steps with groans forced from them by their heavy labour.”<sup>1</sup>

To separate the sulphur from the earthy materials—limestone and gypsum—with which it is mixed, the ore, as in Pliny’s day, is “purified by the agency of fire.” The ore is packed in brickwork furnaces and the charge ignited. The heat developed by the combustion of part of the sulphur serves to melt the rest, which flows down the sloping floor of the furnace and can be run off from time to time. About one-third of the sulphur is thus burned as fuel—but other fuel is scarce in Sicily. In some cases, more especially in Romagna, in Italy, the sulphur is now melted from the ore by superheated steam.

All-important as the Sicilian sulphur production was during and down to the end of last century, it has now sunk to a position of very secondary importance.

As early as 1868, the existence was known of great deposits of sulphur in the State of Louisiana, U.S.A. These deposits, 30–40 yards in thickness, were, however, situated at a depth of 700 feet below the surface, and all attempts to mine them by sinking shafts met with failure owing to the presence, in the overlying strata, of quicksands and poisonous gases. In 1891, however, the American engineer, HERMAN FRASCH, conceived the bold idea of melting the sulphur *in situ* by means of hot water, and pumping the molten sulphur to the surface. The project at first was laughed at, but after several years of effort, the process was successfully developed, with the result that at the present day, owing to the adoption of the Frasch process, 80 per cent. of the annual production of sulphur comes from the more recently discovered deposits in Texas, the original deposit in Louisiana having now become exhausted.

In theory, the Frasch process is very simple. A boring is made through the surface layers down to the bottom of the sulphur-bearing stratum, and in the bore-hole is inserted a nest of concentric pipes (Fig. 68), the outermost of which ends in the cap-rock above the sulphur-bearing stratum. This is a casing-tube, designed to insulate the inner tubes from the surrounding earth. Water heated under pressure to a temperature of about 155° C. is forced down the second outermost tube into the sulphur-bearing stratum, and the sulphur is thereby melted and collects at the bottom of the layer. By the pressure of the water assisted

<sup>1</sup> E. Molinari: *Treatise on General and Industrial Chemistry*. Translated by E. Feilmann. Vol. I.

by hot compressed air passed in through the central tube, the molten sulphur is forced to the surface, where it is run into a large wooden vat. Here the sulphur solidifies, forming a great block of solid sulphur two hundred and fifty feet or more in length. The sulphur has a purity of 99.5 per cent.

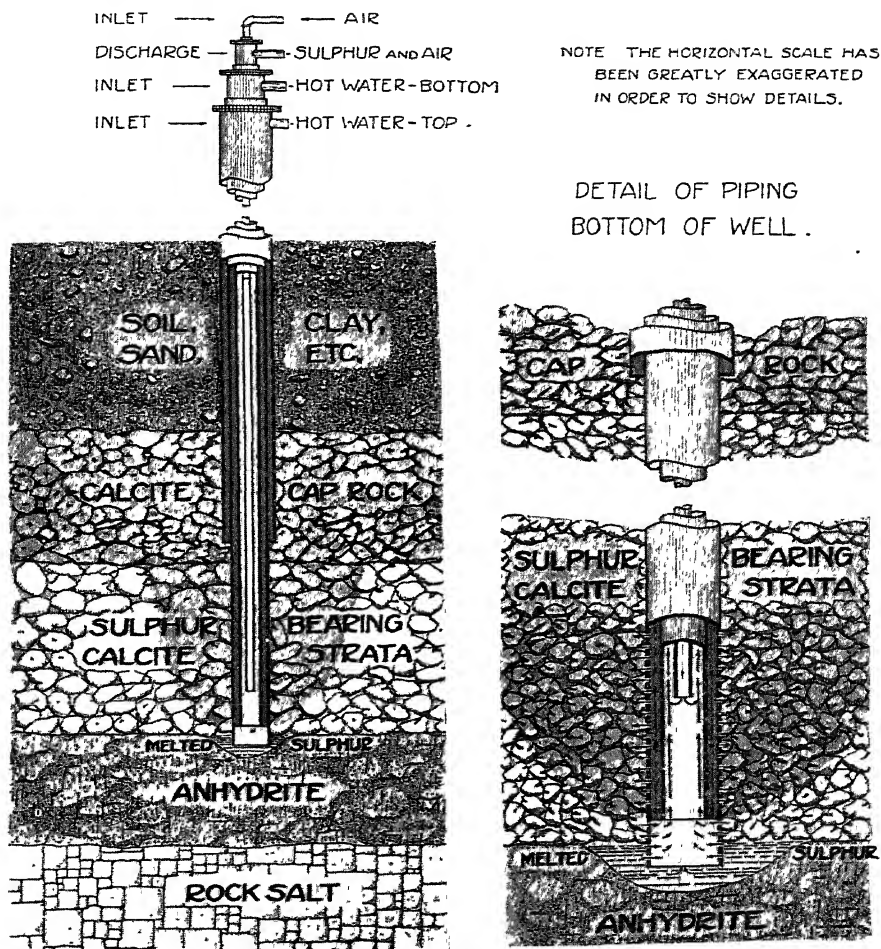
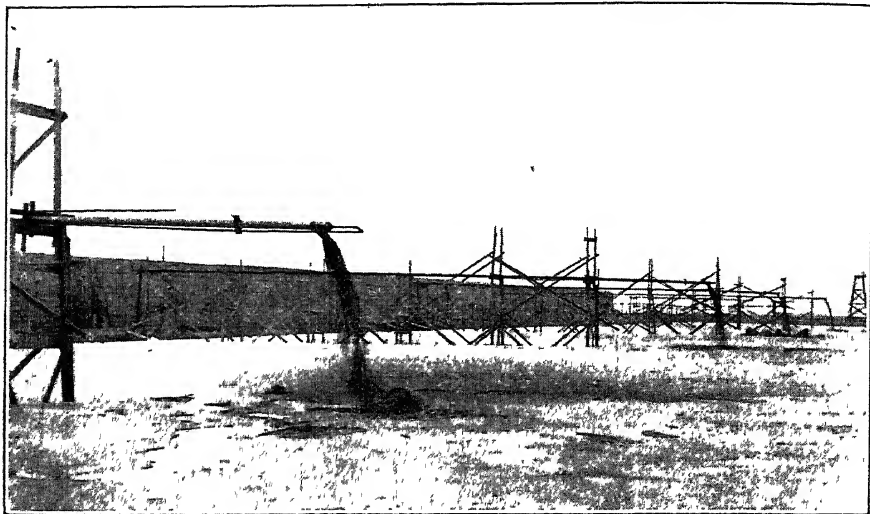


FIG. 68.—Frasch method of winning sulphur.

The refining of crude sulphur is carried out by boiling the sulphur in a retort and leading the vapour into a condensing chamber, where it condenses in the form of a fine powder known as *flowers of sulphur*. When the condensing chamber is small, the walls soon become heated and the sulphur vapour then

condenses to a liquid which is generally run off into cylindrical wooden moulds. In this way one obtains *roll sulphur* or *brimstone*.

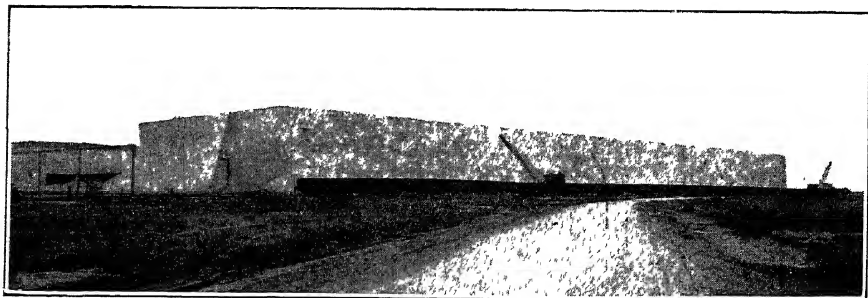
**Allotropy of Sulphur.**—The element sulphur is of interest by reason of its many varied allotropic forms—it is said to have



(Courtesy Texas Gulf Sulphur Co.)

Molten sulphur being pumped into vat.

been obtained in eight different crystalline forms. In nature, sulphur is found in compact *rhombic* crystals (Fig. 69), and these can also be obtained by crystallising sulphur from solu-



(Courtesy Texas Gulf Sulphur Co.)

Loading sulphur into trucks.

tion, say, in carbon disulphide. These rhombic crystals are the form in which sulphur is stable at all temperatures up to  $96^{\circ}$  C. Above this temperature, the rhombic crystals pass,

very slowly, however, into another crystalline form known as *monoclinic* sulphur (Fig. 70). The monoclinic crystals are best



FIG. 69.—Rhombic crystals of sulphur.  
(*British Museum.*)



FIG. 70.—Monoclinic crystals of sulphur.

obtained by melting sulphur in a crucible, and allowing it to cool. The crust which forms on the surface is cut away and the still liquid sulphur poured out. A mass of clear crystalline needles (monoclinic crystals) will be found in the interior. If these crystals are kept at the ordinary temperature, it will be found that in the course of a day or so, they become opaque, owing to their conversion into a large number of rhombic crystals—the stable form, as was pointed out, at temperatures below  $96^{\circ}$ . The change which takes place is analogous to the passage of white tin into grey tin at temperatures below  $13^{\circ}$ . In the case of sulphur, however, the change takes place more readily.

In considering the passage from the liquid to the solid state (Chap. VIII), it was pointed out that a liquid might, under certain conditions, be cooled down far below its ordinary crystallising point and so be obtained as a glassy solid. The production of such a supercooled liquid, as it is called, can be readily effected with sulphur, for if sulphur be heated to its boiling-point and then poured into cold water, it is obtained as a clear, rubber-like mass, which is known as *plastic sulphur*. At the ordinary temperature, however, spontaneous crystallisation sets in, and the clear plastic sulphur passes in time into an opaque mass formed of innumerable crystals of rhombic sulphur.

**Hydrogen Sulphide.**—It has already been pointed out that the family relationship existing between sulphur and oxygen shows itself, for example, in the formation of hydrogen sulphide,  $\text{H}_2\text{S}$ , a compound analogous to water,  $\text{H}_2\text{O}$ , in composition. In its specific properties, however, hydrogen sulphide, still very commonly called by its older name *sulphuretted hydrogen*, differs very markedly from water, for it is, under ordinary conditions, a colourless gas, the malodorous properties of which are probably known to all from the fact that it is formed in the putrefactive decomposition of protein and other sulphur-containing organic substances. Hence the term “smell of rotten eggs,” by which the odour of hydrogen sulphide is generally characterised.

To the ancient Egyptian craftsmen, also, the fetid smell of hydrogen sulphide must have been familiar, and frequent reference is made by Zosimos to the unpleasant odour of the “sulphur water” or solution of calcium sulphide which the Egyptian craftsmen prepared by boiling slaked lime with sulphur, and which they doubtless used for the surface colouring of metals. From such a solution the carbon dioxide of the air liberates hydrogen sulphide. The chemical nature of hydrogen sulphide, called by him “stinking sulphur air,” was first investigated by Scheele about 1773; and it was by Scheele that



the present-day method of preparing the gas, by the action of dilute hydrochloric or sulphuric acid on ferrous sulphide,<sup>1</sup>  $\text{FeS}$ , was introduced.

Hydrogen sulphide is a poisonous gas when inhaled. It is moderately soluble in water and occurs in certain mineral waters, such as those at Strathpeffer, Harrogate and Aix-les-Bains. It is a very valuable reagent in analytical chemistry.

**Sulphur Dioxide and Sulphurous Acid.**—Although it had been known from very early times that an acid-tasting, choking gas is produced when sulphur burns, it was not till 1774 that the great experimenter, JOSEPH PRIESTLEY, by using mercury in place of water in his pneumatic trough, succeeded in isolating the gaseous sulphur dioxide. It was by an accident, moreover, that he was led to the most convenient method of preparing the gas.

Having prepared a quantity of sulphur dioxide (or vitriolic acid air, as he called it), by heating oil of vitriol (sulphuric acid,  $\text{H}_2\text{SO}_4$ ) with olive oil, Priestley attempted to obtain the gas by heating oil of vitriol alone in a special stoppered flask, fitted with a delivery tube (Fig. 71). But although no sulphur dioxide was obtained by this means, yet, as Priestley records, "air was produced at the same time in a manner that I little expected, and I paid pretty dearly for the discovery it occasioned. Despairing to get any air from the longer application of my candles, I withdrew them; but before I could disengage the phial from the vessel of quicksilver, a little of it passed through the tube into the hot acid; when, instantly, it was all filled with dense white fumes, a prodigious quantity of air was generated, the tube through which it was transmitted was broken into many pieces . . . and part of the hot acid being spilled upon my hand, burned it terribly, so that the effect of it is visible to this day."<sup>2</sup>

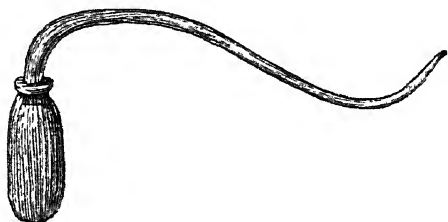
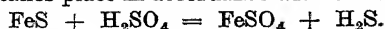


FIG. 71.—Priestley's flask for sulphur dioxide.

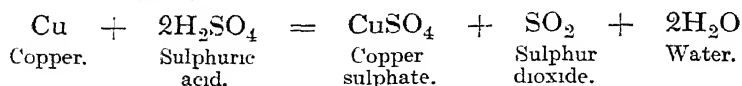
The next day, Priestley heated oil of vitriol with a small amount of mercury and obtained an abundant evolution of sulphur dioxide; and was similarly successful when, instead of

<sup>1</sup> Obtained by heating a mixture of sulphur and iron filings. The production of hydrogen sulphide takes place in accordance with the equation:



<sup>2</sup> Priestley: *Experiments and Observations on Different Kinds of Air*, Vol. II.

mercury, he used the metal copper. This method, discovered by Priestley, is the one by which sulphur dioxide is still generally prepared, in small amounts, in the laboratory (Fig. 72), the reaction being represented by the equation :



Sulphur dioxide is readily liquefied, the liquid being placed on the market in glass bottles and steel cylinders. As the latent heat of evaporation of the liquid is large, sulphur dioxide is sometimes used for refrigeration purposes in place of liquid ammonia (p. 122).

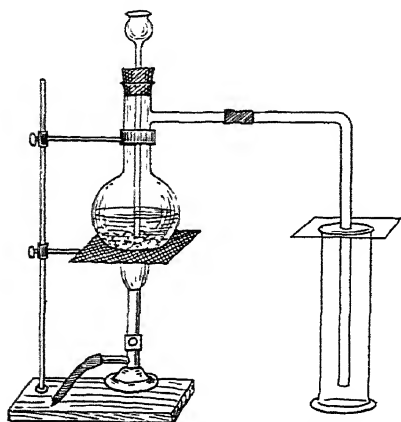


FIG. 72.—Preparation of sulphur dioxide.

Copper turnings are heated in a flask with concentrated sulphuric acid introduced through the thistle funnel. The gas is collected by "downward displacement."

Sulphur dioxide readily dissolves in water, and, as the solution has an acid reaction, it is inferred that the sulphur dioxide combines with water to form the compound *sulphurous acid*,  $\text{H}_2\text{SO}_3$ . This acid, it is true, has never been isolated, but by neutralising the acid solution with alkalis, crystalline salts, known as *sulphites* (e.g. sodium sulphite,  $\text{Na}_2\text{SO}_3$ ), can be obtained. The calcium salt, as will be pointed out later, is used in large amounts in the production of wood pulp.

As has been known from an early period, a solution of sulphurous acid, or sulphur dioxide in presence of moisture, has the property of bleaching animal and vegetable dyes—fruit stains, for example, can be readily removed by its means—and it is largely employed for bleaching silk, wool and other materials which would be destroyed by chlorine bleaching. As is recorded by Pliny, burning sulphur (sulphur dioxide) was used for fumi-gating wool to make it "white and soft."

#### SULPHURIC ACID

Although, owing to the introduction of new processes in chemical manufacture, the importance of sulphuric acid may have somewhat diminished, this acid still remains the most

important chemical reagent in industry. It is by far the most important acid known, and there is scarcely an industry or trade in which it does not find application. It is used in the production of hydrochloric acid, nitric acid and most other acids; in the production of ammonium sulphate and of superphosphate, for use in agriculture; in the refining of petroleum; for cleaning or "pickling" steel plates previous to tinning or galvanising; in electrical storage batteries; in the manufacture of glucose; in the dyeing, calico printing and tanning industries; and in the manufacture of dyes, explosives and many other industrial products. So widespread, in fact, are its applications that some have been prompted to claim that the consumption of sulphuric acid may be taken as an index of the industrial prosperity of a country. At the present day, the world production of sulphuric acid amounts to about 10,000,000 tons.

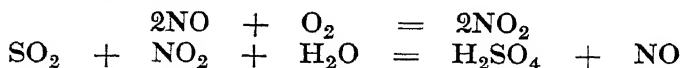
When and by whom sulphuric acid was first prepared is not definitely known, but, although the acid may have been known as early as the eighth century, its preparation by heating green vitriol or ferrous sulphate ( $\text{FeSO}_4$ ) and by burning a mixture of sulphur and nitre (potassium nitrate) in presence of water, is first described in works published in the seventeenth century under the pseudonym of BASIL VALENTINE, a supposititious monk of the fifteenth century. GLAUBER, also, in the seventeenth century, describes the production of a "corrosive oil of vitriol" by the distillation of ferrous sulphate.

The reaction on which the production of sulphuric acid depends is the oxidation of the gas sulphur dioxide to form the compound, sulphur trioxide ( $\text{SO}_3$ ), which combines readily with water to give sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The difficulty is met with, however, that combination between sulphur dioxide and oxygen does not take place appreciably at the ordinary temperature and only slowly even at  $400^\circ \text{C}$ .; and when one seeks to hasten the combination by raising the temperature, another difficulty is encountered. As the temperature is raised the rate at which the sulphur dioxide and the oxygen combine certainly increases, as we have already learned to be universally the case, but as the temperature rises the *extent* to which combination takes place becomes less and less, by reason of the fact that at high temperatures the sulphur trioxide decomposes again into sulphur dioxide and oxygen. One is, in fact, dealing here with what has been called a reversible reaction; and since the formation of sulphur trioxide from sulphur dioxide and oxygen is accompanied by an evolution of heat, it follows—in accordance with the theorem of Le Chatelier—that the higher the temperature, the

smaller is the proportion of sulphur trioxide in the equilibrium mixture. The consequence, therefore, is that at a temperature at which the combination of sulphur dioxide and oxygen takes place sufficiently rapidly (say,  $900^{\circ}$ – $1000^{\circ}$  C.), the amount of sulphur trioxide formed is too small to allow of the process being commercially successful. We now know, however, the direction in which to look for a way out of the difficulty. A catalyst must be found which will so accelerate the rate of oxidation of the sulphur dioxide that the process may be carried out with sufficient rapidity at a temperature so low that the decomposition of the sulphur trioxide is negligible.

At an early date, such a catalyst was found—although it was not, of course, recognised as such—in the oxides of nitrogen. In the year 1740, the manufacture of sulphuric acid was begun at Richmond, near London, by a quack doctor of the name of WARD, who heated a mixture of sulphur and saltpetre in large glass vessels, containing a little water, a method which, as has been pointed out, had been known on the Continent at least a century earlier. Later, in 1746, small lead boxes were substituted by Dr. JOHN ROEBUCK, of Birmingham, for the glass vessels, and other improvements in the process were thereafter introduced, until the present chamber process was evolved. In America, the manufacture of sulphuric acid was started by JOHN HARRISON, of Philadelphia, as early as 1793.

**The Lead Chamber Process.**—The method of manufacturing sulphuric acid by what is known as the lead-chamber process, consists essentially in passing sulphur dioxide, air (oxygen) and oxides of nitrogen into a series of large lead chambers, into which also a fine spray of water is injected. Here, the sulphur dioxide combines with the oxygen of the air under the catalytic influence of nitric oxide, NO, which acts as a transfer catalyst. That is to say, the nitric oxide combines with the oxygen of the air to form nitrogen peroxide,  $\text{NO}_2$ , and the nitrogen peroxide then transfers the oxygen thus taken from the air, to the sulphur dioxide, so as to form sulphur trioxide. This then combines with water to form sulphuric acid. In this process, then, there is alternate oxidation of nitric oxide to nitrogen peroxide by the oxygen of the air, and reduction of nitrogen peroxide to nitric oxide by sulphur dioxide, the cycle of reactions being represented by the two equations :



The sulphuric acid is allowed to collect on the floor of the

lead chambers until the concentration reaches 65–70 per cent. (so-called *chamber acid*), when it is run off, since acid of higher concentration would dissolve the lead of the chambers. The acid may be concentrated by evaporation in silica pans or by blowing hot gases through a spray of the acid.

Until about 1835, the sulphur dioxide used in sulphuric acid manufacture was obtained, almost entirely, by the combustion of Sicilian sulphur; but the great rise in price which followed on the granting of a monopoly of export of Sicilian sulphur, led the manufacturers of sulphuric acid to seek for a cheaper source of sulphur dioxide. This was found in iron pyrites ( $\text{FeS}_2$ ), enormous deposits of which occur more especially in Spain, and in spent iron oxide, used for the purification of coal gas (p. 213); and until the early years of the present century, these materials were the chief sources of sulphur dioxide in sulphuric acid manufacture. In later years, they were augmented by other sulphide ores. As has been pointed out, these various sulphide ores yield sulphur dioxide when heated in a current of air, and large amounts of sulphuric acid are now being produced as a by-product in the extraction of copper, lead and zinc from their respective ores. Although, in Europe, pyrites and spent oxide still constitute the main source of supply of sulphur dioxide, in America the great expansion which has taken place since 1910 in the production of sulphur in Louisiana and Texas, has once more placed the element in a dominant position in sulphuric acid manufacture.

**The Contact Process.**—Up to the beginning of the present century, sulphuric acid was produced almost entirely by the lead-chamber process. The successful development, however, of the industry of synthetic dyes, and more especially the manufacture of synthetic indigotin (the blue colouring matter of indigo), which necessitates the use of the very powerful reagent known as fuming sulphuric acid or “oleum,” led to a widespread use of the so-called *contact process*. At the present day, this fuming sulphuric acid is extensively used in the manufacture of dyes and explosives, and in refining petroleum.

As far back as the year 1817, it was suggested by Sir Humphry Davy that platinum might be employed to accelerate the oxidation of sulphur dioxide by oxygen, just as this metal accelerates the combination of hydrogen and oxygen; and in 1831, practical application of this suggestion was made by a vinegar manufacturer of Bristol, PEREGRINE PHILLIPS by name. Great hopes were aroused for the success of this method of manufacturing sulphuric acid, and even in 1835 a well-known French chemist,

CLEMENT-DESORMES, gave expression to the conviction that in ten years at most it would be possible to manufacture sulphuric acid directly from its constituents, without the use of leaden chambers and nitric acid. But the unwisdom of prophecy is proverbial, and the period of ten years lengthened out to one of nearly seventy before the ability and persistence of the technical chemists in one of Germany's greatest chemical works succeeded in developing the discovery of Peregrine Phillips into a successful industrial process.<sup>1</sup>

When the attempt was made to utilise the "contact process," as it is called, for the commercial production of sulphuric acid, using iron pyrites as the source of sulphur dioxide, a difficulty was met with which delayed success and threatened complete failure. The production of sulphur trioxide which at first took place with great readiness soon began to diminish, and after some time ceased altogether. The platinum lost its catalytic activity. On investigation, this loss of activity was found to be due to a "poisoning" of the platinum—a phenomenon to which reference has already been made—and the substance which was found to be chiefly responsible for this was arsenic. This arsenic was derived from a small amount of impurity contained in the iron pyrites, used as the source of the sulphur dioxide, and it was only after much labour that a means was found of ridding the gas of all traces of this poison. When this had been done the contact process could be carried out with success.

For the production of sulphuric acid by the contact process, the enormous leaden chambers, with a capacity sometimes of 150,000 cubic feet, are replaced by comparatively small, cylindrical vessels containing a suitable catalyst. For this purpose, finely divided platinum is generally used, the platinum being deposited on asbestos (platinised asbestos) or on a porous magnesium sulphate. Complex vanadium silicates, however, which are much less costly than platinum, and the efficiency of which is very great and is not destroyed by arsenic or hydrogen chloride, are now coming into more widespread use as catalysts. Through the reaction vessels, which are maintained at the proper temperature (about 450° C.), by the heat given out in the reaction, the mixture of sulphur dioxide and oxygen (or air) is passed. The oxidation of the sulphur dioxide takes place rapidly and practically completely in presence of the catalyst, and the sulphur

<sup>1</sup> On a restricted scale, Squire and Messel, in England, and certain manufacturers in Germany, manufactured oleum by the contact process, from 1875 onwards. They obtained the sulphur dioxide by the combustion of sulphur or by the decomposition of sulphuric acid on hot brick surfaces or in platinum stills. The oleum so prepared was too costly except for special purposes.

trioxide issues from the apparatus as a white mist, which is then passed into a solution of sulphuric acid containing about 98 per cent. of acid. In this way a pure sulphuric acid, as well also as the powerful fuming sulphuric acid or "oleum" to which we have referred, can readily be obtained.

Whether the contact process will eventually succeed in entirely superseding the older leaden-chamber process, it is impossible to say; for, under the stimulus of competition, improvements have been effected in the latter process, with the result that acid of the concentration mainly required can be produced more cheaply by the chamber than by the contact process, the latter process being used chiefly for the production of "oleum."

**Properties of Sulphuric Acid.**—Concentrated sulphuric acid is a thick, oily liquid which has a very great avidity for water. It is, therefore, largely used as a drying or desiccating agent for the purpose of removing moisture from gases and from solids. In the latter case the solid is placed in a closed vessel or *desiccator*, the interior of which is kept dry by the presence of concentrated sulphuric acid (Fig. 73). It has also a very corrosive action on animal and vegetable matter, and if brought in contact with the skin produces painful and serious burns. Sugar, paper, cloth, etc., are charred and destroyed by it.

At the present time the main use to which sulphuric acid is put is for the production of what is called *superphosphate*, the chief phosphatic fertiliser in agriculture. Probably about 6,000,000 tons of chamber acid are used for the production of about 13,000,000 tons of superphosphate.

Before the year 1840, the phosphorus which is essential for healthy plant growth and which is found mainly in the seeds, was added to the soil chiefly in the form of crushed bones, the phosphorus being present in these as calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , the calcium salt of phosphoric acid,  $\text{H}_3\text{PO}_4$ .<sup>1</sup> Between 1840 and 1850, however, JOHN BENNET LAWES (1814–1900)<sup>2</sup> showed that the

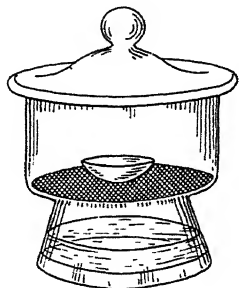


FIG. 73.—Desiccator.

A layer of concentrated sulphuric acid is placed at the bottom of the desiccator and the substance to be dried on a wire gauze support.

<sup>1</sup> Since calcium is bivalent, one atom of calcium can take the place of two atoms of hydrogen, and therefore three atoms of calcium take the place of six atoms of hydrogen present in two molecules of phosphoric acid.

<sup>2</sup> Landowner, chemical manufacturer and founder, in 1843, of the Agricultural Experimental Station, at Rothamsted, Hertfordshire. For his services to agricultural science he was created a baronet by Queen Victoria in 1882.

phosphate could be rendered more readily soluble in the soil and therefore more readily available as a plant food by treating the ground bones with sulphuric acid. The so-called normal calcium phosphate is thereby converted into acid calcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ , and gypsum is formed at the same time.<sup>1</sup> To the mixture of acid calcium phosphate and gypsum the name *superphosphate* was given. Soon thereafter, deposits of mineral phosphate (phosphate rock) were discovered, and since about 1890 almost all the superphosphate has been produced from mineral phosphate. About 60 per cent. of the world's supply of mineral phosphate comes from the enormous deposits in French North Africa (Tunis, Morocco, Algeria) and about 30 per cent. from America (especially Florida).

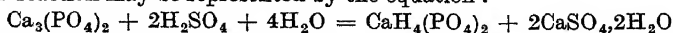
In Germany, America and elsewhere, the production of another phosphate fertiliser is being developed which may perhaps largely supersede superphosphate. By the method already described (p. 175), phosphorus is produced from mineral phosphate; and the phosphorus so obtained is converted to phosphoric acid by means of steam at a high temperature. The hydrogen which is thereby liberated is used for the production of ammonia, by a method to be described later, and the ammonia is combined with the phosphoric acid to form ammonium phosphate. The method is still in its infancy, and time alone can show whether it will develop to maturity.

The salts of sulphuric acid are known as *sulphates*, and may be obtained by the action of dilute sulphuric acid on the metals, or on the oxides, hydroxides or carbonates of the metals. Some of these sulphates occur in nature, and of these one of the most important is *gypsum* or hydrated calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

This substance may occur in chalk-like formations or as a compact and marble-like material, known as *alabaster*.<sup>2</sup> It is a soft material which is easily worked, and is frequently used for making ornamental objects, statuettes, etc.

One of the most important and oldest uses to which gypsum is put is for making a plaster or moulding material, now known as *plaster of Paris*. As such, it was made use of by the Egyptians even at a very early date. Plaster of Paris is readily obtained by carefully heating gypsum to a temperature somewhat above the boiling-point of water. About three-quarters of the water with which the calcium sulphate is combined is driven off, and

<sup>1</sup> The reaction may be represented by the equation :



<sup>2</sup> The term alabaster is also applied, in Egyptology, to a compact crystalline form of calcium carbonate.



on grinding the product, a white powder is obtained which when mixed to a paste with water, quickly sets to a hard mass. The explanation of this is that the partially dehydrated gypsum (plaster of Paris) combines with water and forms the hydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Plaster of Paris is used for making casts, for interior wall mouldings (stucco), for application to the soil, and for surgical bandages.

Other well-known sulphates are Glauber's salt or sodium sulphate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), copper sulphate and magnesium sulphate or Epsom salts ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ).

## CHAPTER XXII

### SALTS OF POTASSIUM AND SODIUM

Just as the metals sodium and potassium, the two most important members of the natural family of the so-called *alkali metals*, resemble each other in their physical properties, so also do they give rise to compounds of a similar character. Potassium hydroxide, KOH, or caustic potash, for example, is similar in its properties to sodium hydroxide and may be prepared in a similar manner, namely, by the electrolysis of an aqueous solution of potassium chloride, KCl. Potassium chloride, potassium sulphate ( $K_2SO_4$ ), and potassium carbonate ( $K_2CO_3$ ), likewise, are similar to the corresponding sodium salts, but potassium bicarbonate differs notably from sodium bicarbonate in being much more readily soluble in water. Although similar in their general properties, the two series of salts differ in the properties which depend on the sodium or potassium present in the compound, so that, for certain purposes, *e.g.* in agriculture, the place of potassium salts cannot be taken by the salts of sodium.

**Salts of Potassium.**—The salts of potassium are of very great importance because of the fact that they are essential for the healthy growth of all land plants, and must be added in sufficient quantity to the soil if a vigorous cultivation is to be maintained. More especially are potassium salts of importance in the cultivation of cereals, potatoes, beet, vines and cotton; and the banana plant responds in a most surprising fashion when manured with potash salts. When land vegetation is burned, the potassium which the plants had taken up from the soil, is recovered in the ash in the form of potassium carbonate ( $K_2CO_3$ ), this salt being obtained by lixiviation of the ash with water, evaporation of the solution and calcination of the residue in pots. Hence the name *pot-ash* for potassium carbonate. For long, the potash so obtained constituted the main source of supply of that material which was required not only in agriculture, but also in the glass, soap and other industries. In the middle of last century, indeed, nearly three-quarters of the world's supply of potash came from

the wood ashes of the lumber camps of Canada. At the present time, nearly all the potash salts used are of mineral origin.

Lying on an enormous layer of rock salt (sodium chloride), which extends widely through North and Middle Germany, great beds of potassium and other salts are found at various points, and more especially in the neighbourhood of Stassfurt, a town situated some twenty miles southwards from Magdeburg. Here, even as early as the thirteenth century, brine springs were known, but it was not till about 1852 that the deep-lying deposits of rock salt began to be mined. The minerals lying in layers above this bed of rock salt, and having an aggregate thickness



(Courtesy Sir John Russell)

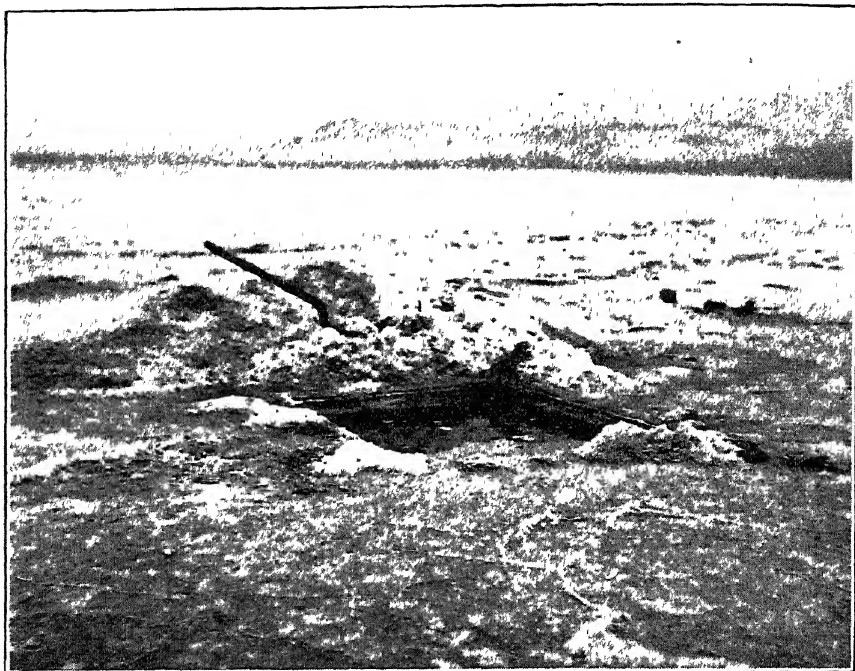
Effect of potash salts on growth of mangolds

The root on the left has been grown in soil to which a potash fertiliser has been added; that on the right, in a soil containing no potash.

of over five hundred feet, were rejected as useless until they were recognised as being a valuable source of potassium and magnesium salts.

These vast deposits of salts, extending over an area of about one hundred square miles, were formed, as it is calculated, over a period of some eight millenniums, by the evaporation of sea-water flowing intermittently into an inland basin, just as at the present day similar salt-beds are being laid down in the Bay of Adj-Darja, in the East of the Caspian Sea. In these deposits are to be found not only the salts of sodium, calcium and magnesium, but also great quantities of potassium salts, of which the best known and most important are *sylvine* or potassium

chloride (KCl), *kainite*, a complex salt containing both potassium and magnesium ( $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$ ), and *carnallite* ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ). These deposits have, more especially since 1880, been worked in a most systematic and scientific manner, and they form by far the largest and cheapest source of the agriculturally vital potassium compounds. The crude salts may be used as potash fertilisers or the potash salts may be extracted and purified by crystallisation from water. To learn



Searles Lake, California.

Below the crust of salts there lies a saturated brine from which potassium chloride and borax are extracted

how this can best be effected, required very long and laborious investigations of the solubilities of the different salts in presence of one another. These investigations were carried out mainly by VAN'T HOFF and his pupils.

Although the most important so far discovered, the Stassfurt deposits are not the only deposits of potash salts. In 1904, salt deposits were discovered in Alsace, occupying an area of some seven square miles to the north-east of Mulhouse. In these deposits, estimated to contain 300,000,000 tons of potash,

the potash is present mainly as potassium chloride. The exploitation of the deposits is easy and the purification of the potassium chloride from the accompanying rock salt is a simple process compared with that to which the Stassfurt deposits must be subjected. The production of potash salts from these Alsatian mines is, however, regulated in agreement with the German producers.

In America, large quantities of potash salts occur in the brine and salt lakes of California and Nevada ; and at Searles Lake, in the Mojave desert, California, potassium chloride is being successfully produced in large amount.

Although other sources of potash salts are known to exist, *e.g.* the flue dust from blast-furnaces and cement works, and the giant seaweeds, more especially of the Pacific, their exploitation, in normal times, has so far not proved economically successful.

**Potassium Nitrate and Sodium Nitrate.**—Potassium nitrate ( $\text{KNO}_3$ ), nitre or saltpetre is a salt which, from the manner of its formation and occurrence, may have been known at an early time, for it is formed by the bacterial decomposition in the soil of waste nitrogenous animal matter (excreta, urine). In warm countries, more especially, such as India, Persia and Arabia, this process takes place with great readiness, and in the neighbourhood of the dwellings where the sanitary arrangements are of a primitive character, the ammoniacal compounds formed by the decomposition of waste animal matter are converted by the nitrifying bacteria to nitric acid, which forms potassium nitrate or calcium nitrate with the potash salts or lime present in the soil. By the addition of wood ashes (potassium carbonate), the calcium nitrate is converted to potassium nitrate and calcium carbonate. The nitrates are extracted from the soil by water.

Potassium nitrate was not at first clearly distinguished from naturally occurring soda, to which the term nitre was applied. At a later time the name saltpetre<sup>1</sup> was given to the salt on account of the fact that, having been formed in the manner just described, it could be extracted from the soil and from certain rocks.

The most important use to which saltpetre was put in the past and is put in the present, is in the manufacture of *touch paper* and of rapidly burning materials such as black *gunpowder*. As early as the seventh century, we read,<sup>2</sup> a rapidly burning mixture, known as Greek Fire, was used by the inhabitants of Constantinople in their defence of the city against the Moslems, and, even

<sup>1</sup> From the Latin *sal petrae*, salt of the rock.

<sup>2</sup> Gibbon, *Decline and Fall of the Roman Empire*, Chap. 52.

as late as the thirteenth century, rapidly burning mixtures of sulphur, pitch, naphtha and other substances, which "came flying through the air like a winged long-tailed dragon, about the thickness of a hogshead, with the report of thunder and the velocity of lightning," were used by the Moslems in the Crusades. Whether in this Greek Fire saltpetre was present is not known, but about the same time the Chinese appear to have employed saltpetre in the manufacture of a sort of gunpowder, which was used for explosive toys and for fireworks. By the thirteenth century, in any case, saltpetre had been introduced from China into Europe by the Arabs, under the name of "China salt," and its use for the production of "flying fire" was well known. Thus, the composition of a mixture not differing greatly from black gunpowder is given in the *Book of Fires* or *Liber Ignium ad comburendos Hostes*, written under the name of "MARCUS GRÆCUS," in the thirteenth century. Roger Bacon also appears to have known of gunpowder, which is said to have been first used for firearms at Florence in 1325, and was first used in fieldpieces by the English at the battle of Crécy in 1346, when the guns "threw little balls of iron to frighten the horses."

*Gunpowder*, the composition of which may vary slightly, is a mixture of about 75 per cent. of potassium nitrate or saltpetre, 14 per cent. of charcoal and 11 per cent. of sulphur. Its action as an explosive and as ammunition for firearms depends on the rapid combustion of the charcoal and sulphur at the expense of the oxygen contained in the saltpetre, with production of gases (especially nitrogen and carbon dioxide), the volume of which is many times that of the solid gunpowder. Solid substances are also produced and make smoke. The pressure produced by the gas is very greatly increased by the great elevation of temperature brought about by the heat of combustion of the gunpowder, and actual tests have shown that when gunpowder is fired in a closed space, a pressure of upwards of four hundred atmospheres is produced.

While still largely used in connection with the beneficent operations of mining and also for pyrotechnic displays, gunpowder is no longer employed as a propellant for naval or military purposes. Its use has been given up not only on account of the large amount of smoke produced in the explosion, which acts as a screen and prevents the effective use of quickfiring guns, but also because, as we shall learn presently, explosives of very much greater power and efficiency have been discovered.

After the introduction of gunpowder for use in firearms, the saltpetre necessary for its manufacture was obtained mainly

from India, where the *sorawallahs*<sup>1</sup> carried on the business of extracting the saltpetre from the earth collected in the neighbourhood of native dwellings and cowhouses; and in certain European countries *nitre plantations* for the production of nitre from waste nitrogenous animal matter, were established to supply local needs. In France, during the wars of the Revolution, 2000 tons of saltpetre were produced annually in such plantations. Later, in 1855, the demand for gunpowder, occasioned by the out-

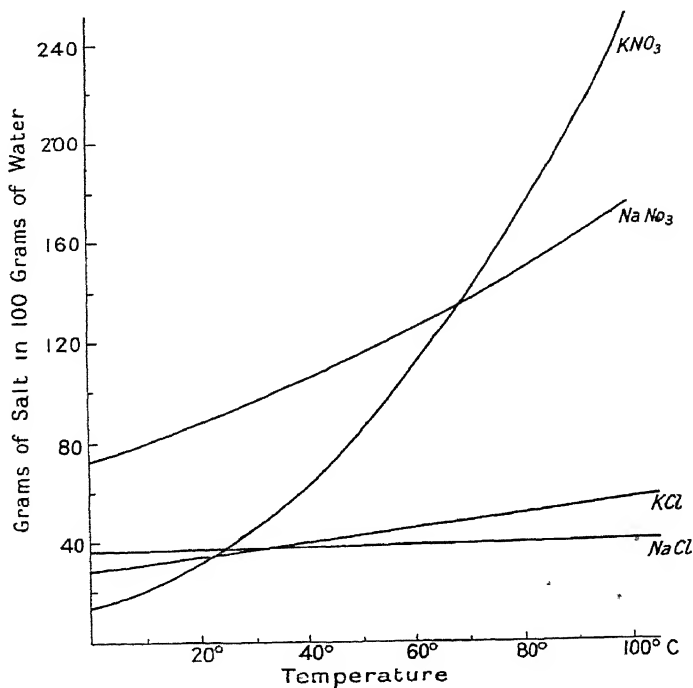


FIG. 74.—Solubility curves of the chlorides and nitrates of potassium and sodium.

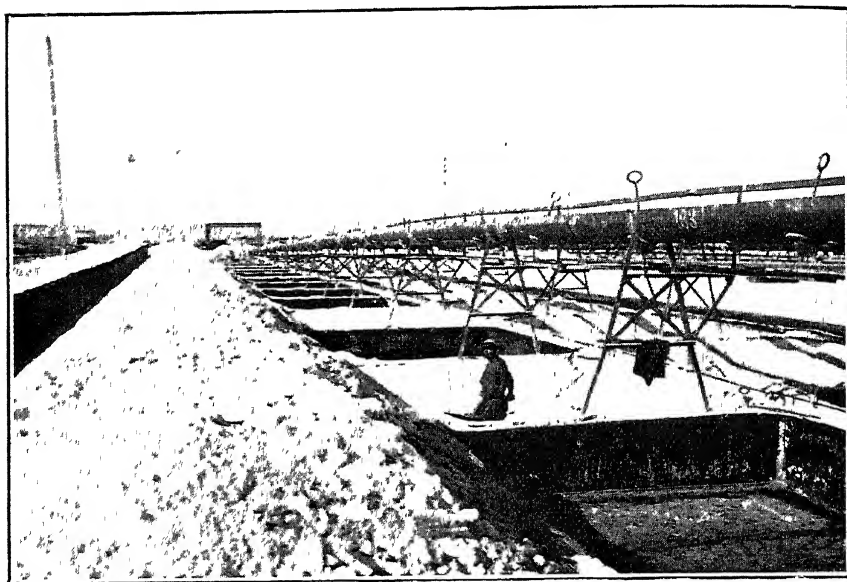
break of the Crimean War, led to the development of processes for the conversion of sodium nitrate<sup>2</sup> or Chile saltpetre ( $\text{NaNO}_3$ ), into potassium nitrate by reaction with potassium salts; and at the present day, most of the potassium nitrate is produced by reaction between potassium chloride and sodium nitrate, as shown by the equation:  $\text{KCl} + \text{NaNO}_3 = \text{KNO}_3 + \text{NaCl}$ .

On examining the solubility curves (p. 236) of these four salts, as shown in Fig. 74, it will be seen that at 100° C., 247 grams of

<sup>1</sup> That is, nitre workers, from *sora*=nitre.

<sup>2</sup> Sodium nitrate cannot be used for the manufacture of gunpowder because it deliquesces or becomes moist on exposure to the air.

potassium nitrate dissolve in 100 grams of water, whereas at  $0^{\circ}$ , only 13 grams dissolve. In the case of sodium chloride, the solubility changes only slightly with the temperature; at  $0^{\circ}$ , 35.7 grams, and at  $100^{\circ}$ , 39.1 grams, of sodium chloride dissolve in 100 grams of water. When, therefore, potassium chloride and sodium nitrate are mixed together with water at, say,  $100^{\circ}$ , so as to give an almost saturated solution of potassium nitrate, most of the sodium chloride separates from the solution while the saltpetre remains dissolved. On cooling down the solution, after addition of a small amount of water to prevent the further



(Courtesy The Chilean Nitrate Committee)

Chile saltpetre. Emptying the crystallisation tanks.

separation of sodium chloride, the greater part of the potassium nitrate separates out, by reason of its small solubility at low temperature.

About 1825, enormous deposits of *caliche*<sup>1</sup> or impure sodium nitrate were discovered in the rainless districts of the Tarapaca and Atacama deserts of Chile; and after 1850, these deposits rapidly increased in importance as the Chile saltpetre or sodium

<sup>1</sup> *Caliche* may vary considerably in composition, but consists essentially of earthy matter along with various salts, especially sodium nitrate, sodium chloride and sodium sulphate. A number of other salts are present in smaller amounts, and of these, sodium iodate, the chief source of iodine at the present day, is the most important.



nitrate, extracted from the *caliche*, became increasingly used not only for the production of nitric acid and potassium nitrate, but more especially as one of the most important nitrogenous fertilisers in agriculture.

From the mixture of salts present in *caliche*, the sodium nitrate is obtained by leaching the *caliche* with hot water and allowing it to crystallise out from the solution on cooling.

**Sodium Carbonate.**—One of the most important salts of sodium, manufactured in very large quantity at the present day and used for the softening of water, in the manufacture of soap and glass, and for other purposes, is *sodium carbonate* ( $\text{Na}_2\text{CO}_3$ ) or *soda*.

Sodium carbonate has been known from remotest ages as forming a deposit<sup>1</sup> on the floor and shores of the soda-lakes of Egypt; and these were probably the chief source from which the early Phœnician traders obtained the salt. Soda occurs abundantly in certain waters and lakes, *e.g.* Lake Magadi, in Kenya, and Owen's Lake, California, from the water of which soda can be obtained by solar evaporation. These natural soda deposits are again being worked at the present day. Formerly soda was called *natron* or *nitre*, and by this name it is referred to in the Bible.<sup>2</sup>

Previous to the nineteenth century, the carbonate of soda required, more especially, for the manufacture of glass and of soap, to which reference will be made later, was obtained mainly from the soda-lakes or from the ash of the saltwort (*Salsola kali* L.). This was grown on large areas reclaimed from the sea along the coast of Spain, and more especially along the coast of Alicante, and was reduced to ash by ignition. This ash, containing up to 15 or 20 per cent. of sodium carbonate, was sold under the name of *barilla*.<sup>3</sup> The supply, however, was scanty, and barely sufficient to meet the demand. There was, therefore, great need for an abundant source of cheap soda. After it had been discovered by the French chemist HENRI LOUIS DUHAMEL DU MONCEAU (1700–1781), that soda is derived from the same base

<sup>1</sup> The natural "soda" or *trona*, as it is called, is the compound known as sodium sesquicarbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ . When this is heated water and carbon dioxide are driven off and the normal sodium carbonate obtained:  $2(\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}) = 3\text{Na}_2\text{CO}_3 + \text{CO}_2 + 5\text{H}_2\text{O}$ .

<sup>2</sup> "As he that taketh away a garriant in cold weather, and as vinegar upon nitre, so is he that singeth songs to a heavy heart" (Proverbs xxv. 20). Soda, when acted on by vinegar (acetic acid), is decomposed with brisk effervescence due to the production of carbonic acid gas.

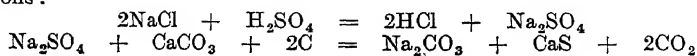
<sup>3</sup> The *barilla* industry was introduced into Spain by the Saracens, who called the saltwort, or the ash of saltwort, *al gali* or *al kali*. From this the term alkali is derived. On the salt steppes of the Argentine, the saltwort is still grown, and burned for the production of soda.

as common salt, the artificial production of soda from common salt became possible. On account of the great economic importance of soda, the Academy of Paris, in 1775, offered a prize for a process of converting common salt, or chloride of sodium, of which there are such abundant supplies occurring naturally, into the carbonate of sodium or soda; and the problem was solved by the French chemist NICOLAS LEBLANC (1742-1806), in 1791. A factory for the manufacture of soda by the Leblanc process was started near Paris, but was soon afterwards confiscated by the Committee of Public Safety. Although the factory was handed back to Leblanc in 1801, he had no capital with which to restart; and after some years of struggle, filled with despair, the inventor of a process which has contributed so much to the comfort and well-being of the people by giving to them cheap glass and cheap soap, ended his days by his own hand.

The process invented by Leblanc consists of several stages. Salt, first of all, is heated with sulphuric acid, whereby the chloride of sodium is converted into sulphate of sodium or "salt-cake," as it is called commercially. At the same time there are produced large quantities of hydrogen chloride or hydrochloric acid gas, HCl. This reaction, we have seen, was known at least as early as the time of Glauber in the seventeenth century. The salt-cake is then heated with a mixture of limestone (calcium carbonate) and coal, whereby the sulphate of soda is converted into carbonate of soda, which can then be extracted by means of water.<sup>1</sup> The residue, consisting mainly of sulphide of calcium, and known as alkali waste or soda waste, is left. For long, the accumulations of this soda waste were a source of much annoyance to the community (by reason of the evil-smelling gas, sulphuretted hydrogen, which they evolved), as well as a loss to the manufacturers. After many failures, however, a process was discovered whereby the sulphur present in the waste could be recovered, and the economy which was thereby effected enabled the Leblanc process to maintain itself, at least for a time, against the formidable rival by which, as we shall learn, it was assailed during the latter half of the century.

It was in England, more especially, that the Leblanc process was worked, from 1814 onwards. At first the hydrochloric acid gas which was evolved in the process was discharged into the

<sup>1</sup> The reactions which take place can be conveniently represented by the equations:

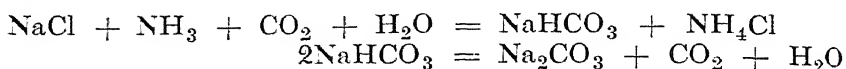


air and became an intolerable nuisance, by reason of the fact that it destroyed all the vegetation in the neighbourhood of the works, and rapidly corroded all ironwork. To still the outcry which was raised, more or less successful attempts were made to absorb the gas in water, in which it dissolves with great readiness. But if one trouble was thereby removed, a fresh one arose, and the soda manufacturers found themselves with large quantities of hydrochloric acid, for which there was scarcely any use, and which could not be run into the rivers as it would kill the fish. A way out of the difficulty, however, was at length discovered, and the hydrochloric acid, which had been a source of annoyance to the community and of worry to the manufacturers, became a source of considerable profit. In 1868, H. W. DEACON (1822–1877), showed that if the hydrogen chloride, mixed with air, is passed over heated pumice, impregnated with cuprous chloride, the cuprous chloride acts as a catalyst and accelerates the oxidation of the hydrogen chloride by the oxygen of the air, with formation of chlorine (Deacon's process); and by passing the chlorine over slaked lime, bleaching powder is obtained (p. 276). For this bleaching powder a great demand sprang up in the middle of last century, due to the development not only of the cotton but also of the paper industry, the raw materials for which required to be bleached before use. The production of hydrochloric acid played henceforward an important part in the success of the Leblanc process.

Important and successful as was the Leblanc process during the first sixty or seventy years of the nineteenth century, it had by the end of the century practically succumbed before an economically more successful rival, the so-called ammonia-soda or Solvay process. The reaction underlying this process, a reaction between sodium chloride and ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ), giving rise to sodium bicarbonate ( $\text{NaHCO}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ), had been discovered, prior to 1811, by one who later became more famous as a physicist, the Frenchman, AUGUSTIN JEAN FRESNEL (1788–1827). During the first half of the nineteenth century, many industrial chemists in different countries attempted to apply the reaction, but production on an industrial scale was in all cases unsuccessful.

In 1863, however, the Belgian industrial chemist and philanthropist, ERNEST SOLVAY (1838–1922), successfully developed the process whereby soda can be produced more economically and in a purer form than by the method of Leblanc. The process depends on the fact that when carbon dioxide (obtained by heating limestone or calcium carbonate) is passed

into a solution of common salt saturated with ammonia,  $\text{NH}_3$ , (obtained by the distillation of coal or by a synthetic process described in the following chapter), sodium bicarbonate is deposited. By heating the bicarbonate, ordinary sodium carbonate or soda is obtained. The series of reactions, then, are represented by the equations :



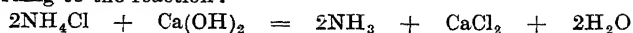
The ammonia is recovered by heating the ammonium chloride with slaked lime,<sup>1</sup> and the carbon dioxide, formed by the decomposition of the sodium bicarbonate, is used over again in the process.

When sodium carbonate is crystallised from water, it forms hydrated crystals, sodium carbonate decahydrate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , known popularly as *washing soda*. On the other hand, sodium bicarbonate, as has been pointed out, readily gives rise to carbon dioxide on being heated, and for this reason it is largely employed, under the name of *baking soda*, in the preparation of baking powders. By the evolution of carbon dioxide in baking, the dough is made lighter.

**Sodium Chloride.**—The commonest and most abundant compound of sodium, the source of nearly all the other salts of the metal and of the metal itself, is common salt or *sodium chloride*,  $\text{NaCl}$ . This substance is an essential constituent of the food of man and the animals, and although, in many places, primitive man must have been unacquainted with salt, the need of it was not felt so long as man lived on milk and the raw or roasted flesh of animals. When, however, in the process of civilisation, man ceased to be a nomadic hunter and became a settled farmer and adopted a diet of cereals, vegetables and boiled meat, salt became a necessity. Henceforward, salt was held in special esteem by men and came to be regarded as “divine,” a “substance dear to the gods”; and to eat of a man’s salt created a sacred bond of loyalty and friendship. A valuable article of commerce, trade routes were constructed for its distribution, and the possession of sources of supply even became the cause of war.

Common salt forms over 70 per cent. of the salts present in sea-water—in each gallon of which about a quarter of a pound of sodium chloride is present—and it is found, very abundantly, both as rock salt and in salt wells, in many countries of the world. Of the deposits of rock salt, the most famous is that at

<sup>1</sup> According to the reaction :



Wielicza in Galicia, where salt has been mined since the twelfth century. Here passages and chambers extend for thirty miles, and great halls adorned with glittering columns have been cut in the enormous mass of rock salt.

At one time salt was obtained almost entirely by the solar evaporation of sea-water, or the water of salt lakes ; and even at the present day considerable quantities are still so obtained in Spain, France, Italy, United States (California and the Great Salt Lake, Utah) and other countries which enjoy a dry climate. Most of the salt of commerce is, however, now obtained by evaporation in pans of the naturally occurring brine or the brine obtained by dissolving rock salt in water. By varying the manner in which the crystallisation of the salt is caused to take place, salt crystals of varying degrees of fineness are produced. Rapid evaporation, at the boiling-point, for example, accompanied by agitation of the solution, causes the salt to separate in the finely crystalline form desired for table-salt.

## CHAPTER XXIII

### NITROGEN. THE PRODUCTION OF FERTILISERS AND EXPLOSIVES

OF all the chemical elements of which our text-books describe the properties, none, perhaps, was, until a comparatively short time ago, so uninteresting as nitrogen. From the time of its discovery by the botanist RUTHERFORD in 1772 (p. 145), down to the end of the nineteenth century, scarcely a character or property of a positive nature was ascribed to the element. Its properties were negative properties, and were described in negative terms. Useless when alone, it did not readily enter into reaction with its fellow-elements; and it played, at best, the rôle—again negative in character—of acting as a drag on the too vigorous activity of the atmospheric oxygen.

That an important part in the economy of nature has, nevertheless, been assigned to this element, is abundantly clear from the fact that it is an essential constituent of the most important animal and vegetable materials (protoplasm, proteins), a constituent without which life itself is impossible. Moreover, a number of very important mineral compounds of nitrogen have long been known, such as saltpetre or potassium nitrate ( $\text{KNO}_3$ ), sal ammoniac or ammonium chloride ( $\text{NH}_4\text{Cl}$ ), and nitric acid ( $\text{HNO}_3$ ), so that, however uninteresting the element itself may appear to be, its compounds have played a part of considerable importance in the economy of nature and in the progress of civilisation.

**Nitric Acid.**—In a work belonging to the thirteenth century and written in Latin under the name (possibly a pseudonym) of GEBER, the preparation of what is now called nitric acid, by strongly heating in an alembic or retort a mixture of saltpetre, alum and copper sulphate, is described; and in the seventeenth century, GLAUBER describes its preparation by heating saltpetre and sulphuric acid. The importance of nitric acid was early recognised by the alchemists, who found that it readily dissolves metals like lead, copper and silver which are attacked with difficulty by hydrochloric and sulphuric acids, and they

gave to this valuable reagent, therefore, the name *aqua fortis*. By its means, silver could be separated from gold. It was, moreover, found that if, in the preparation of nitric acid, sal ammoniac or common salt was added to the saltpetre in the retort, a liquid—which one now knows was a mixture of hydrochloric and nitric acids—was obtained which would even dissolve gold; and because of its solvent power on the king of metals, this liquid was called *aqua regia*. By the thirteenth century, then, chemists had become acquainted with the three most powerful acids, hydrochloric, sulphuric and nitric acids, so that a much more rapid development of chemical knowledge could take place than was possible when acetic acid—known in ancient times—was the only acid recognised.

Until early in the present century, nitric acid, whether required for the production of sulphuric acid by the lead-chamber process, or for the manufacture of explosives, was universally prepared by the method of Glauber, except that, after 1830, Chile saltpetre or sodium nitrate was substituted for the more expensive potassium nitrate. On heating sodium nitrate in a retort (Fig. 75), with concentrated sulphuric acid, reaction readily takes place in accordance with the equation :

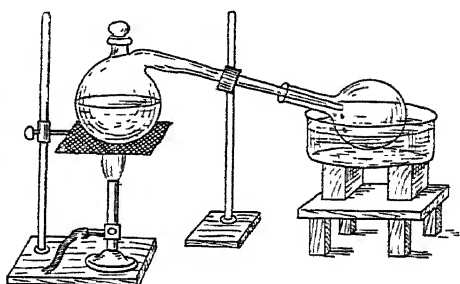
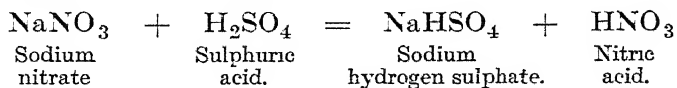


FIG. 75.—Preparation of nitric acid



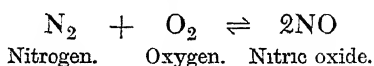
Nitric acid distils over, and can be collected in a cool receiver. The pure acid is colourless, but, owing to the slight decomposition of the nitric acid by heat, with formation of the brown coloured oxide, *nitrogen peroxide* or *tetroxide* ( $\text{NO}_2$  or  $\text{N}_2\text{O}_4$ ), the acid exhibits a slightly yellow colour. Nitric acid is a highly corrosive liquid, which destroys animal and vegetable matter. When diluted with water, it stains skin, silk and wool yellow. It is a powerful oxidising agent.

As long ago as 1784, CAVENDISH showed that when electric sparks are passed through air, oxides of nitrogen are formed through combination of the oxygen and nitrogen; and when these oxides are absorbed in water or in alkalis, nitric acid or

nitrates are obtained. The possibility of obtaining nitric acid from the air was thereby demonstrated. When, therefore, in the closing years of the nineteenth century the "fixation" of atmospheric nitrogen, or the conversion of atmospheric nitrogen into the form of compounds, for use, more especially, as fertilisers in agriculture, appeared to be a matter of importance and even of urgency, it was only natural that attempts should be made by chemists and engineers to apply the scientific fact discovered by Cavendish and to develop it into a commercially successful process.

In this connection it is important to note one respect in which the combustion of nitrogen, or the combination of nitrogen with oxygen, differs from the combustion, say, of hydrogen. When hydrogen burns, a large amount of heat is given out, and consequently, when a mixture of hydrogen and oxygen is ignited at any point, the temperature of the surrounding gas is raised to the ignition point and the flame spreads throughout the whole mixture. In the case of nitrogen and oxygen, however, combination takes place with *absorption* of heat—the reaction is an endothermic one—and heat must therefore be continually added to the mixture in order to allow the process of combustion or combination to proceed. Indeed, if it were not so, a flash of lightning would set the whole atmosphere ablaze, and "deluge the world in a sea of nitric and nitrous acids."

Further, the reaction between nitrogen and oxygen whereby the compound *nitric oxide* is formed, is a reversible reaction (p. 320), represented by the expression :

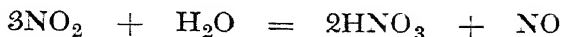


and at a given temperature, therefore, only a partial combination of the gases takes place. It is, however, a general rule (theorem of Le Chatelier) that, in such a case, the reaction which takes place with absorption of heat is favoured by raising the temperature; and it is therefore to be expected that as the temperature is raised, the proportion of nitric oxide produced will become greater and greater. This prediction from theory was confirmed by experiment.

In 1903, the Norwegian physicist, KRISTIAN BIRKELAND (1867–1917), Professor of Physics in the University of Christiania (Oslo), and the engineer, Dr. SAMUEL EYDE, developed an economically successful process for the production of nitric acid from the nitrogen and oxygen of the air. Air was passed into a special furnace in which an electric arc was formed, and at the



high temperature so obtained (about  $3000^{\circ}$  C.), the nitrogen and oxygen combined to form nitric oxide (NO). The gases were then led away from the furnace, rapidly cooled and passed into chambers lined with acid-proof stone, where time was given to the nitric oxide to combine with the free oxygen present in the air and so to form the brown-coloured higher oxide, *nitrogen peroxide*,  $\text{NO}_2$ . On absorbing this gas in water, nitric acid is formed as shown by the equation :



and when oxygen (air) is also present, it combines with the nitric oxide to reproduce nitrogen peroxide, which in turn gives more nitric acid.

It was in Southern Norway, at Notodden and Rjukan, that the process was mainly operative; and there, in 1927, about 38,000 tons of nitrogen were converted into 171,000 tons of nitric acid. This great and romantic undertaking, however, in spite of the success which it achieved, has had to give way before a younger and more lusty rival: and the arc process, the first industrially successful process for the fixation of atmospheric nitrogen, was, after celebrating its semi-jubilee, closed down in 1928. Instead of being used for the production of high temperature arcs, the electrical energy available in Southern Norway will now be utilised for the electrolytic production of hydrogen, which in turn will be used for the production of synthetic ammonia. By the combustion of this compound, as will be discussed more fully later, nitric acid can be obtained.

**Oxides of Nitrogen.**—Besides the compounds, nitric oxide,<sup>1</sup> NO, and nitrogen peroxide,  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$ ,<sup>2</sup> to which reference has just been made, nitrogen can form three other oxides,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_5$ , the last two oxides being the *anhydrides* (the acids minus the elements of water) of *nitrous acid*,  $\text{HNO}_2$ , and *nitric acid*,  $\text{HNO}_3$ , respectively. Nitrogen, therefore, forms a series of no fewer than five oxides, the composition of which was first fully determined by GAY-LUSSAC in 1816. The existence of these oxides forms an excellent illustration of Dalton's law of multiple proportions (p. 56).

<sup>1</sup> On a small scale, nitric oxide is best prepared by the action of nitric acid on copper:  $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$ . The gas may be collected over water.

<sup>2</sup> At low temperatures, this oxide exists mainly as  $\text{N}_2\text{O}_4$  molecules, but as the temperature is raised, the  $\text{N}_2\text{O}_4$  molecules dissociate into  $\text{NO}_2$  molecules. This process is accompanied by a marked deepening of the brown colour.

On analysis, the oxides are found to have the following composition :

	Percentage composition	
	Nitrogen	Oxygen.
Nitrous oxide . . . . .	63·63	36·37
Nitric oxide . . . . .	46·67	53·33
Nitrous anhydride . . . . .	36·84	63·16
Nitrogen tetroxide . . . . .	30·44	69·56
Nitric anhydride . . . . .	25·93	74·07

If, from these numbers, one calculates how much oxygen is combined with a definite amount, say, 100 parts by weight, of nitrogen, it is found that these amounts are 57·15, 114·3, 171·5, 228·5, 285·7 respectively. These numbers, it is found, are in the ratio 1 : 2 : 3 : 4 : 5.

**Nitrous Oxide.**—When JOSEPH PRIESTLEY, in 1772, allowed nitric oxide (NO), which he had just discovered, to stand in contact with a mixture of iron filings and sulphur, he found that the volume of gas diminished, and that the nitric oxide, in which a candle would not burn, had been converted into a gas in which “a candle burned with an enlarged flame.”

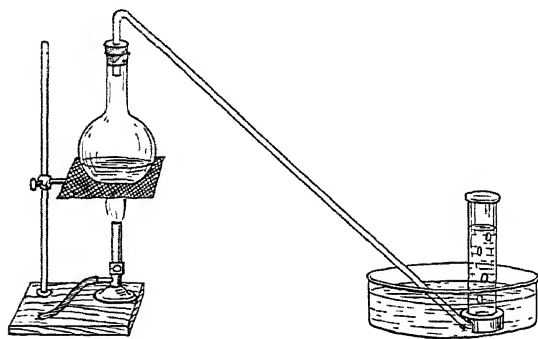
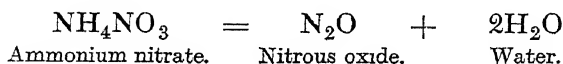


FIG. 76.—Preparation of nitrous oxide

could also be obtained by the action of zinc on dilute nitric acid. This gas, the properties of which were first studied by Priestley, is now known as *nitrous oxide* ( $N_2O$ ), and is most conveniently prepared in a pure state, by carefully heating ammonium nitrate (Fig. 76).

This fact was first discovered in 1785 by the French chemist, CLAUDE LOUIS BERTHOLLET, along with PIERRE SIMON DE LAPLACE, who later became famous as a mathematician and astronomer, the decomposition being represented by the equation :



As the gas is fairly readily soluble in cold water, it is best collected in a pneumatic trough over hot water, or over brine.

Twenty-four years after the discovery of nitrous oxide, the view was advanced by that very remarkable man, SAMUEL LATHAM

MITCHILL (1764–1830), Professor of Natural History, Chemistry and Agriculture, at Columbia University, New York, that nitrous oxide, or oxide of septon as he called it, is the cause of all contagious diseases and is able to produce the most horrible effects when it is inspired or even brought in contact with the skin. This extraordinary theory might, perhaps, have had no more effect on the progress of science than that of a breeze ruffling the surface of the sea, if it had not been that, in Cornwall, about the same time, an English boy, HUMPHRY DAVY, had become interested in chemistry. In 1798, Davy, who was at that time apprenticed to a surgeon-apothecary in Penzance, became acquainted with Mitchill's theory, and he forthwith prepared some nitrous oxide and proceeded to test the theory experimentally. In recording his results, he stated: "Wounds were exposed to its action, the bodies of animals were immersed in it without injury; and I breathed it mingled in small quantities with common air, without remarkable effects." The results of experiment did not accord with the theory. In the following year, being then installed at the Medical Pneumatic Institution at Bristol, Davy resumed the investigation of nitrous oxide, and he laid the foundation of his scientific career, which came to mean so much for the advance of chemical science, by his discovery of the property of nitrous oxide of producing, when inhaled, a nervous exaltation, followed, on more prolonged inhalation, by anæsthesia. From the fact that the state of exaltation was sometimes accompanied by involuntary laughter, the gas was popularly called "*laughing gas*." The discovery is referred to by the authoress, Maria Edgeworth, a sister of Mrs. Beddoes, in the following passage:

"A young man, a Mr. Davy, at Dr. Beddoes', who has applied himself much to chemistry, has made some discoveries of importance, and enthusiastically expects wonders will be performed by the use of certain gases, which inebriate in the most delightful manner, having the oblivious effects of Lethe, and at the same time giving the rapturous sensations of the Nectar of the Gods! Pleasure even to madness is the consequence of this draught. But faith, great faith, is, I believe, necessary to produce any effect upon the drinkers, and I have seen some of the adventurous philosophers, who sought in vain for satisfaction in the bag of 'Gaseous Oxyd,' and found nothing but a sick stomach and a giddy head."

The discovery of the physiological action of nitrous oxide created something of a sensation, and, although the properties of the gas as an anæsthetic (especially in dental surgery) were

not made use of until a much later time, the intoxicating and exhilarating action of the gas induced many, including the poets Southey<sup>1</sup> and Coleridge, to seek "satisfaction in the bag of gaseous Oxyd"—not always, it is gathered, with the desired result.



Laughing Gas

(Illustration by G. Cruikshank from Scoffern's *Chemistry No Mystery*.)

"Some jumped over the tables and chairs; some were bent upon making speeches; some were very much inclined to fight; and one young gentleman persisted in an attempt to kiss the ladies "

<sup>1</sup> Southey, on one occasion, describes his sensations on inhaling nitrous oxide, as follows: "My first definite sensation was a dizziness, a fulness in the head, such as to induce a fear of falling When I took the bag from my mouth, I immediately laughed The laugh was involuntary but highly pleasurable, accompanied by a thrill all through me; and a tingling in my toes and fingers, a sensation perfectly new and delightful Certain I am that I felt myself more than normally strong and cheerful "

Nitrous oxide, which resembles oxygen in its power of supporting combustion, can be distinguished from this gas by its failure to react with nitric oxide, NO. When oxygen is mixed with nitric oxide, the brown gas, nitrogen peroxide,  $\text{NO}_2$ , readily soluble in water, is formed; but no such action is given with nitrous oxide.

**Ammonia.**—Even at a very early time, the term *sal ammoniacum* was applied to the common salt or soda, or mixtures of these which were found in the Libyan Desert, in the neighbourhood of the temple of Jupiter Ammon; but at a much later date, perhaps about the twelfth or thirteenth century, the name became generally used for the salt which is now known as sal ammoniac or ammonium chloride,  $\text{NH}_4\text{Cl}$ .

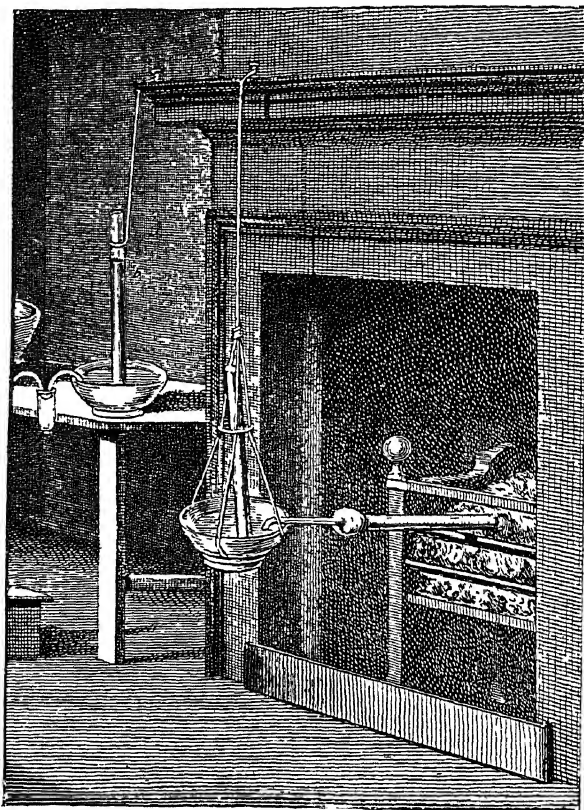
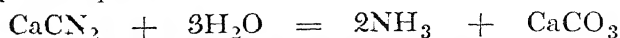
In 1727, it was observed by STEPHEN HALES, who was, as has been mentioned, the inventor of the pneumatic trough, that when sal ammoniac was heated in a retort along with lime, in an apparatus such as is represented in Fig. 12, p. 97, no gas collected, but water was sucked into the retort. A number of years later, about 1772, Priestley succeeded in collecting an alkaline gas by repeating the experiment of Hales, using mercury, however, in his pneumatic trough in place of water. The gas is very soluble in water, and to it BERGMAN, in 1782, gave the name ammonia. A solution of ammonia in water had long been known under the name of *spirits of hartshorn*, so called because it is obtained by heating in a closed retort, horns, hoofs and other nitrogenous matter; and, in fact, until the time of Priestley, ammonia was known only in the form of its solution. The solution has an alkaline reaction, and it is therefore inferred that ammonia combines to some extent, at least, with water so as to form ammonium hydroxide,<sup>1</sup>  $\text{NH}_4\text{OH}$ . On neutralising these solutions with acids, salts are obtained, such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ .

It has already been pointed out that when coal is distilled in retorts for the production of gas or coke, considerable quantities of ammonia are obtained; and until 1913, this was by far the most important source of ammonia and of its salts. The ammonia so produced was, for the most part, converted into sulphate of ammonia or ammonium sulphate, by means of sulphuric acid and was used as a nitrogenous fertiliser.

About 1906, a process was introduced for the purpose of utilising atmospheric nitrogen for the production of ammonia. This process depends on the fact that when nitrogen is passed

<sup>1</sup> The "radical" or group of atoms,  $\text{NH}_4$ , which acts like an element, is known as ammonium.

over calcium carbide,  $\text{CaC}_2$ , a substance which is used in large quantities for the production of acetylene (p. 218), suitably heated in retorts, a reaction takes place with formation of a compound known as calcium cyanamide,  $\text{CaCN}_2$ .<sup>1</sup> By heating this compound with steam, under pressure, ammonia is formed, as shown by the equation :



Priestley's apparatus for collecting gases over mercury

The nitrogen required for the production of calcium cyanamide is obtained by the distillation of liquid air, and the above process is therefore really one whereby ammonia is produced indirectly from the nitrogen of the air and the hydrogen of water.

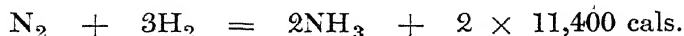
Interesting and important as was the process which has just been described for the production of ammonia from atmospheric nitrogen, there is one other reaction which attracted the attention

<sup>1</sup> According to the equation :  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ .

of chemists from the moment when the importance of an increased production of nitrogenous compounds for use in agriculture became apparent. This is the direct synthesis of ammonia from nitrogen and hydrogen. It had, for a considerable time, been well known that nitrogen and hydrogen combine under the influence of the electric discharge, but the amount of ammonia produced was very small; and it was also known that the reaction between nitrogen and hydrogen is a reversible one, and leads, therefore, to a state of equilibrium. The concentration of ammonia, at the temperature employed, is exceedingly small, and all attempts to obtain an appreciable amount of the compound by direct combination of nitrogen and hydrogen ended in failure.

In the closing years of the nineteenth century, however, new weapons had been forged—the weapons of chemical dynamics and of catalysis—and it was realised that no success could be obtained in the industrial production of synthetic ammonia until the chemical dynamics of the reaction had been submitted to a systematic and exact investigation. This investigation was carried out, about 1905, under the guidance and direction, more especially, of the German chemist, FRITZ HABER, at that time Professor of Chemistry at the Technical High School of Karlsruhe, and, since 1911, Professor of Physical Chemistry in the University and Director of the Kaiser Wilhelm Institute of Physical Chemistry and Electrochemistry, Berlin. By 1909, the scientific foundation on which an industrial process might be erected was laid, and in 1913, the industrial production of ammonia, by direct synthesis from nitrogen and hydrogen, was begun in Germany.

The equation for the combination of nitrogen and hydrogen to form ammonia, namely :



shows that 1 gram-molecule of nitrogen combines with 3 gram-molecules of hydrogen to form 2 gram-molecules of ammonia; or, if one takes the volume at N.T.P. of 1 gram-molecule (22,400 c.c.) as unit volume, one may say that one volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. In other words, combination of nitrogen and hydrogen is accompanied by a diminution of volume, and therefore, according to the laws of chemical dynamics,<sup>1</sup> the proportion

<sup>1</sup> According to the theorem of Le Chatelier, a reaction which takes place with diminution of volume is facilitated or favoured by increase of pressure; whereas, a reaction which takes place with increase of volume, is favoured by diminution of pressure.

of ammonia or the concentration of ammonia at equilibrium will be increased by allowing the gases to react under a high pressure. Moreover, since the combination of nitrogen and hydrogen takes place with *evolution* of heat, the production of ammonia will, in accordance with the theorem of Le Chatelier (p. 322), be favoured by keeping the temperature low. These predictions from theory were borne out by experiment, as the following table shows :

Temperature.	Percentage amount of ammonia in the equilibrium mixture when the pressure was	
	1 atmosphere.	100 atmospheres.
800° C. . . . .	0.011	1.1
700° C. . . . .	0.021	2.1
600° C. . . . .	0.048	4.5
500° C. . . . .	0.13	10.8

In order, therefore, to attain success in the industrial synthesis of ammonia from its elements, the rule must be borne in mind : Maintain the gases under as high a pressure and at as low a temperature as possible.

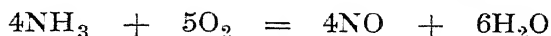
In this case, as in other cases, however, one encounters that factor which so sharply distinguishes success in the scientific laboratory from success in the factory, the factor of time. At 500° C., it is true, quite an appreciable proportion of ammonia is formed by the direct combination of hydrogen and nitrogen, but the *rate* at which the ammonia is produced is so slow that the process would be industrially useless. By the use of a suitable catalyst, however, such as oxide of iron to which potassium oxide, molybdenum, aluminium oxide or other substances are added as promoters (p. 325), the reaction velocity can be satisfactorily increased ; and the synthetic production of ammonia has been added to the industries of the world. About 600,000 tons of atmospheric nitrogen are now converted annually into ammonia, the amount of ammonia so obtained being far in excess of that produced by the distillation of coal ; and the production is rapidly increasing.

**Use in Refrigeration.**—Ammonia is a colourless gas which is very soluble in water, and it is in the form of its aqueous solution, long spoken of as *spirits of hartshorn*, that it is best known. With its pungent smell, every one is familiar. Although a gas under ordinary conditions, ammonia can easily be liquefied by a comparatively slight increase of pressure and lowering of temperature, as was, in fact, shown by FARADAY in 1823 ; and owing to the fact that the liquid has a high latent heat of evaporation (p. 120), it is extensively employed for the production of ice and for purposes of general refrigeration. This may be effected in the following manner : Ammonia, liquefied by pressure,



circulates through pipes immersed in a tank of brine and is caused to boil under reduced pressure. The latent heat of evaporation is abstracted from the brine, which is thereby cooled down to a low temperature, and the cold brine is then circulated through the refrigeration chambers. Or, ice may be formed by placing metal containers filled with water in the cold brine.

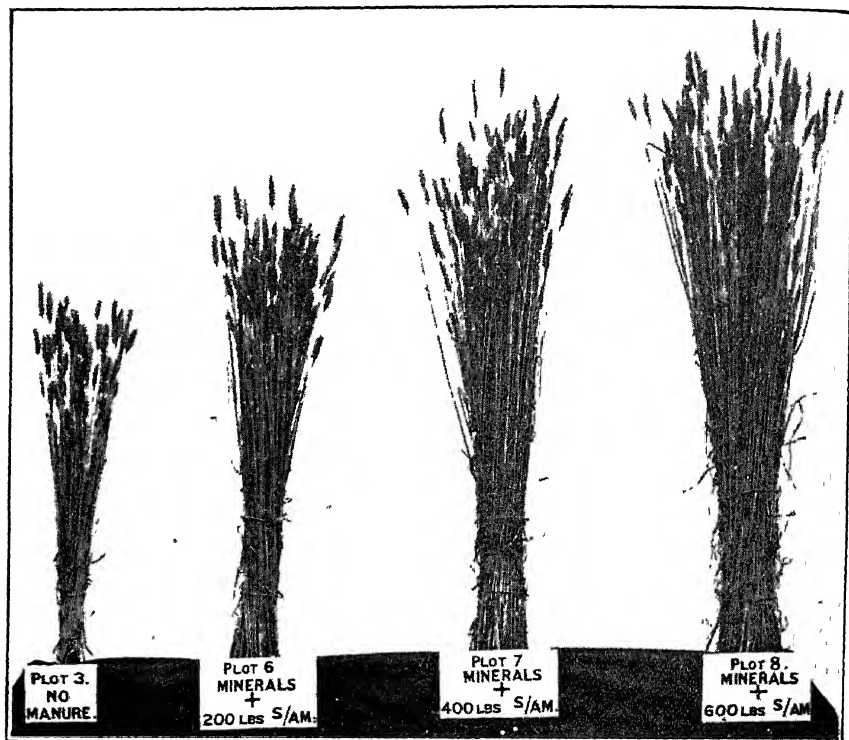
**Nitric Acid from Ammonia.**—Although ammonia burns readily in oxygen, it does not, under ordinary conditions, burn in air. If, however, a mixture of air and ammonia is passed over platinum, generally in the form of fine wire gauze, heated to a temperature of about  $800^{\circ}\text{C}$ ., the platinum acts as a catalyst and accelerates the combustion of ammonia. In this process, nitric oxide is formed as represented by the equation :



This apparently very simple reaction is one of exceedingly great economic importance, for, as has already been pointed out, nitric oxide combines directly with the oxygen of the air to form nitrogen peroxide ( $\text{NO}_2$ ), which when absorbed in water gives rise to nitric acid. By the oxidation of ammonia, therefore, it is possible to obtain the substance, nitric acid, which above all others is indispensable in the manufacture of modern explosives. The importance of the above process will be realised when one recalls that previous to 1913, all countries were dependent on Chile saltpetre for the production of nitric acid, and a country therefore could, in time of war, be rendered powerless by cutting off its supplies of Chile saltpetre. It was, in fact, under the stimulus of the apprehension that such might be the fate of his country, that the German chemist, WILHELM OSTWALD, addressed himself to the task of developing into a successful industrial process the oxidation of ammonia to nitric acid. It was in 1913 that Germany established the synthetic production of ammonia on an industrial scale, and in the later years of the Great War she obtained through that process and through the catalytic oxidation of the ammonia, all the ammonium nitrate and nitric acid which she required for use in explosives and in the manufacture of explosives. Besides being used for the production of nitric acid, the catalytic combustion of ammonia is now also being used, to an increasing extent, for the production of the nitric oxide required as catalyst in the manufacture of sulphuric acid.

**Nitrogenous Fertilisers.**—It was the German chemist, JUSTUS VON LIEBIG (1803–1873), who first, in 1840, pointed out that plants do not subsist merely on the water and carbon dioxide

which they abstract from the air and the soil, but that they have to be fed with the elements necessary for the building up of their structures. No fewer than about thirteen elements are required by plants, and of these, the most important are nitrogen, phosphorus and potassium. One ton of wheat, it is stated, abstracts from the soil 47 lbs. of nitrogen, 18 lbs. of phosphoric acid and 12 lbs. of potash. Phosphorus, we have seen, is added to the soil in the form of basic slag, superphosphate or ammonium



(Courtesy Sir John Russell)

Effect of nitrogenous fertilisers (ammonium sulphate) on plant growth.

phosphate, and potassium in the form of potassium chloride or potassium sulphate. In the case of nitrogen, it is found that certain plants, such as peas, beans, alfalfa, clover and other leguminous plants, are able, through the symbiotic action of colonies of bacteria occurring in nodules on the roots of the plant, to take up elementary nitrogen from the air, and such plants, therefore, enrich the soil; but in other cases, combined nitrogen must be added to the soil in a form which the plants can assimilate.

Owing to the apparent impossibility of coaxing the enormous store of elementary nitrogen contained in the air into suitable combination with other elements, mankind contented itself, resignedly if not complacently, with the natural sources of supply of useful nitrogen compounds; and this position was all the easier to adopt as the natural supply was sufficient for the needs of the day. In 1898, however, Sir WILLIAM CROOKES, as President of the British Association, delivered the solemn warning that the years of plenty were quickly passing. The supply of wheat, the staple foodstuff of Western peoples, from all the land available for cultivation, would soon be insufficient to provide for the needs of the growing population unless the yield of the soil could be greatly increased by intensive cultivation; and this, in its turn, would, in a few years, exhaust all the known sources of combined nitrogen. Famine, therefore, stared them in the face, and there would be no Egypt from whose granaries supplies could be obtained.

Apart from animal manures, which had only a local importance, agriculture depended for its supply of nitrogen fertilisers mainly on the ammonia produced as a by-product in the distillation of coal and on Chile saltpetre or sodium nitrate. Although it was clearly a matter of importance to recover, as far as possible, the ammonia which is produced in the carbonising of coal, an increase in the amount of coal distilled, such as would afford an adequate supply of nitrogenous fertilisers, was economically impracticable; and while it was quite feasible to increase very greatly the production of Chile saltpetre, it had to be borne in mind that the nitrate deposits, although enormous, are not inexhaustible. It is obvious, therefore, that the situation in 1898 was one which might well cause grave concern to men of foresight and vision, unless fresh sources of supply of the indispensable nitrogen compounds could be secured. As the discovery of new supplies of naturally occurring nitrogen compounds, in any considerable quantity, was not to be relied on, there was an imperative demand laid on chemists to discover some means of forcing the inexhaustible store of elementary nitrogen into such a state of combination that its assimilation by plants would be rendered possible. As Sir William Crookes said: "The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists." And the ingenuity of chemists, assisted by the engineers, has, as we have seen, proved amply equal to the task. Since 1903, three methods (to mention only the most important) have been discovered by which atmospheric nitrogen can, on a large scale

and in a commercially successful manner, be forced into useful combination with other elements. These processes are, as we have seen, the arc process for the production of nitric acid and nitrates, the calcium cyanamide process, and, most important of all, the direct synthesis of ammonia. As a consequence of these developments, the synthetic nitrogen compounds constituted, in 1927, no less than 56 per cent. of all nitrogenous fertilisers, whereas by-product ammonia constituted only 28 per cent., and Chile saltpetre, 16 per cent. Moreover, while the output from the last two sources remains practically stationary, the production of synthetic ammonia, more especially, is rapidly increasing and can be still further increased to any desired extent.

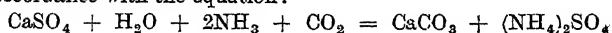
Much of the ammonia which is now produced, by direct combination of nitrogen and hydrogen, is converted into various salts for use in agriculture, and of these the most important is *ammonium sulphate*,  $(\text{NH}_4)_2\text{SO}_4$ . Whereas, formerly, this salt was obtained by combining the ammonia with sulphuric acid, one now finds that both in Germany and in England, the two countries in which synthetic ammonia is chiefly produced, use is made of gypsum or calcium sulphate. If a suspension of finely ground gypsum in water is treated in a closed vessel with ammonia and carbon dioxide,<sup>1</sup> ammonium sulphate and calcium carbonate are formed.<sup>2</sup> The calcium carbonate is used for the production of cement, as will be described later.

**Explosives.**—It has already been pointed out (p. 180) that man's progress towards a higher and more complex civilisation has depended very largely on his ability to utilise, control and direct energy—the energy of chemical change. Material progress, however, depends not only on the amount of energy utilised but also on the extent to which energy can be concentrated, and so man has sought to obtain more and more concentrated forms of energy, for use both in peace and in war. Such highly concentrated forms of energy are found in explosives.

An explosive may be defined as a substance or mixture which is capable of undergoing extremely rapid combustion or decomposition, with production of gaseous substances which occupy a volume many times greater than—perhaps ten or twelve thousand times as great as—the volume of the explosive itself. In the

<sup>1</sup> In Germany and in England the hydrogen required for the ammonia synthesis is obtained from water gas, the carbon monoxide being removed by means of steam and a catalyst (p. 333). In this process, therefore, carbon dioxide is produced and this is used in the above reaction.

<sup>2</sup> In accordance with the equation:



case of gunpowder, the first explosive to be used, one has a mixture of combustible substances (charcoal, sulphur) with a substance (saltpetre) which supplies the oxygen necessary for the combustion. In modern explosives—introduced since the middle of the nineteenth century—we have compounds in the molecule of which is contained the oxygen necessary for combustion, or compounds which are so unstable that when subjected to suitable shock, the molecules break up. In all these compounds the element nitrogen is present, and for their production nitric acid is required.

The investigation of the action of nitric acid on various organic compounds or compounds of carbon, which led to the discovery of modern explosives, followed on the increased and cheapened production of nitric acid resulting from the exploitation and introduction into Europe of Chile saltpetre. Thus, in 1846, SCHÖNBEIN discovered *gun-cotton*, which is produced by the action of a mixture of nitric acid and sulphuric acid on cotton. Cotton consists, essentially, of the chemical substance cellulose, a compound of carbon, hydrogen and oxygen, represented, perhaps, by the formula,  $C_{24}H_{40}O_{20}$ . When this is acted on by a mixture of nitric and sulphuric acids, various compounds of cellulose with nitric acid (cellulose nitrates) are formed. The more highly "nitrated" compounds constitute gun-cotton.

When ignited, loose gun-cotton burns with great rapidity, the oxygen required for the combustion being contained within the molecule of the compound itself. The molecule of gun-cotton, moreover, is in a very unstable condition, and when subjected to a shock, as, for example, when a little fulminate of mercury is caused to detonate near it, it suddenly decomposes and gives rise to a large volume of gaseous substances: nitrogen, oxides of carbon and water vapour. Since these gases are all colourless, and as no solid materials are formed, the explosion of gun-cotton is unaccompanied by smoke.

The fulminate of mercury to which reference has just been made, was discovered in 1799 by EDWARD CHARLES HOWARD (1774–1816), brother of the 12th Duke of Norfolk, by adding alcohol to a solution of mercury in concentrated nitric acid. It is a white crystalline substance, having the formula,  $HgC_2N_2O_2, \frac{1}{2}H_2O$ .

Even as late as the Napoleonic Wars, firearms were discharged by means of sparks struck by flint from steel, but in 1805, a detonating lock was invented by the Aberdeenshire minister, Rev. ALEXANDER JOHN FORSYTH, the detonating mixture consisting of potassium chlorate, charcoal and sulphur.

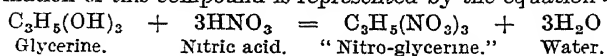
This device, however, was soon displaced by the fulminate of mercury percussion cap, first invented, it is stated, by J. SHAW, of Philadelphia, in 1814.

The explosive or disruptive effect of gun-cotton is very great by reason of the rapidity with which the decomposition of the substance takes place. Thus, whereas a couple of pounds of gunpowder require about a hundredth of a second for complete combustion, the same weight of gun-cotton undergoes decomposition in about one fifty-thousandth part of a second. It is on this fact that the shattering or disruptive effect, the "brisançe," depends. It is this fact also that makes gun-cotton, which is very valuable as a "high" or "disruptive" explosive, unsuitable for use as a "low" or "propulsive" explosive in guns. It would simply burst the gun.

Although gun-cotton cannot be employed as a propellant, the advantages attaching to a smokeless explosive are so obvious, that attempts were made to overcome the difficulties due to the rapid rate of explosion. These attempts to "tame" the gun-cotton have been entirely successful. Although the less highly nitrated "nitro-cottons" are soluble in a mixture of ether and alcohol, forming the liquid *collodion*, gun-cotton is, at most, only partially soluble in this solvent. It can, however, be obtained in a gelatinised state by dissolving it in acetone and evaporating off the solvent. In this gelatinised state, the disruptive properties of the gun-cotton are greatly modified, and such gelatinised gun-cotton can safely be used in firearms, as a smokeless powder.

A further advance in the chemistry of explosives was made in 1847 by the Italian chemist, ASCANIO SOBRERO, Professor of Chemistry in the University of Turin, who found that when glycerine is acted on by nitric acid, a very highly explosive liquid is obtained, known as "nitro-glycerine," or, more correctly, glyceryl nitrate.<sup>1</sup> This substance, first manufactured on a commercial scale in 1862 by the Swedish chemist and engineer, ALFRED BERNHARD NOBEL (1833-1896), founder of the Nobel Prizes, was difficult to handle on account of its great sensitiveness to shock, and was the cause of many fatal accidents. In 1866, however, after prolonged investigation, Nobel discovered that if the liquid nitro-glycerine was mixed with kieselguhr, a fine earth composed of the siliceous skeletons of marine diatoms, it could be transported and handled with comparative freedom

<sup>1</sup> The formation of this compound is represented by the equation :



from danger.<sup>1</sup> This mixture was introduced commercially in 1867 under the name of *dynamite*. Its explosion is initiated by means of a detonator.

In 1875, Nobel produced a new type of explosive by dissolving nitro-cotton in nitro-glycerine, the tough jelly-like mass which is formed being known as *blasting gelatine*. That this explosive is more powerful than dynamite—that it is, indeed, one of the most powerful blasting explosives known—will cause no wonder, since the nitro-glycerine is not mixed with an inactive material like kieselguhr, but with a substance which is itself an explosive.

The British service powder, *cordite*, is prepared by mixing a “paste” of gun-cotton (65 per cent.) and nitro-glycerine (30 per cent.), with acetone, and adding a quantity of vaseline (5 per cent.),<sup>2</sup> and the mixture is then forced by hydraulic pressure through a die into the form of a thread or cord. Hence the name *cordite*. After evaporating off the acetone, the *cordite* forms a horn-like material which is very insensitive to shock and safe to handle. This “taming” action of gelatinisation on two of the most powerful explosives, is one of the most important and remarkable discoveries in this branch of science; and gun-cotton, gelatinised in one way or another, is now the basis of all propulsive ammunition.

Although gun-cotton is extensively employed as a high explosive, more specially in torpedoes, other explosives, derived from the products of distillation of coal, are employed in shells. Of these explosives the two most important and most used are *picric acid* and *trinitrotoluene*.

When carbolic acid ( $C_6H_5.OH$ ), or phenol, to give it its scientific name, is treated with a mixture of nitric and sulphuric acids, there is formed trinitrophenol or picric acid,  $C_6H_2(OH)(NO_2)_3$ . This compound was first obtained by an English chemist, PETER Woulfe (1727–1803), in 1771, but it was not till 1843 that it was prepared from phenol. On account of its bitter taste, the name picric acid<sup>3</sup> was given to the compound by the French chemist, Dumas. As ordinarily obtained, it is a faintly yellow crystalline substance, which has long been used as a yellow dye for silk. It was introduced as an explosive in France in 1885. Picric acid melts to a liquid at a temperature of  $122^\circ C.$ , and in this state it is run into the shell. On account of the honey-yellow colour of the molten picric acid, this substance

<sup>1</sup> Wood-flour or wood-meal, burnt cork, charcoal and other materials are also used as absorbents in place of kieselguhr.

<sup>2</sup> Vaseline lowers the temperature of the explosion and so reduces the erosion of the gun barrel, and it also increases the stability of the *cordite* when stored.

<sup>3</sup> From the Greek *πικρός* (*picros*), bitter.

received from the French the name of *mélinite*, while in England it is called *lyddite*, on account of the fact that it was at Lydd, in Kent, that its use as a high explosive was first tested. In other countries it receives still other names, such as *pertite* (Italy), *dunnite* (U.S.A.) and *schimosite* (Japan). Although picric acid can be handled with perfect safety, its destructive power, when exploded by means of a suitable detonator, exceeds that of gun-cotton or dynamite. Some idea of the enormous amount of potential energy contained in picric acid can be gained from the fact that when a pound of the substance is exploded, it liberates an amount of energy equal to that required to raise a weight of over a ton to a height of more than one hundred yards. Unfortunately, picric acid has the property of forming with metals compounds which are much more sensitive than itself, and so may give rise to untoward accidents. Another explosive, therefore, has come into favour in recent years, a substance derived from the hydrocarbon toluene,  $C_6H_5.CH_3$ , and called *trinitrotoluene* or T.N.T., or *trotyl*. This substance also is a solid, and can be subjected with impunity to very rough usage; a bullet, even, may be fired into the mass without producing any effect. When detonated, however, trinitrotoluene explodes with a violence not much inferior to picric acid, but as the oxidation of the carbon in the compound is by no means complete, dense black clouds of carbonaceous matter are produced, and this led to the nicknames of "Coal-box" and "Black Maria" being applied to the shells filled with this explosive. In order to secure more perfect combustion and, at the same time, to reduce the amount of T.N.T. required, ammonium nitrate, a substance containing an excess of oxygen, is now generally added. In this way the British service high explosive, *amatol*, a mixture of 80 parts of ammonium nitrate with 20 parts of T.N.T., is obtained.

In times of peace no less than in times of war explosives are of great importance; and by rendering possible such great engineering works as the Suez Canal and Panama Canal, and the removal, in 1885, of the reef known as Hell Gate in the channel of the East River, New York, they have played an important part in the peaceful progress of civilisation.



## CHAPTER XXIV

### SILICA, CLAY, LIME AND GLASS

#### SILICA

OF the naturally occurring minerals, one of the first to attract the attention of men and to be used by them for ornamental



Rock crystal.

purposes, was, doubtless, the colourless, highly lustrous *rock crystal*, which is found in many parts of the world in the form of beautiful hexagonal columns, capped by six-sided pyramids.

Even at a very remote time, in ancient Egypt, rock crystal was known, and used for decorative and ornamental purposes. By the early Greek philosophers, who regarded earth and stones as having been formed by the congealing of water, rock crystal was supposed "to be but ice extraordinarily hardened by long and vehement cold" (Boyle). It was called by them, therefore, *crystallos* or *crystal*.<sup>1</sup> It was for long regarded as a simple, elementary substance, and it was only in 1823 that BERZELIUS succeeded in decomposing it, and in showing that it is an oxide



Castle Geyser, Yellowstone Park.

—as Lavoisier had assumed it to be—of an element to which was given the name *silicon*.<sup>2</sup>

*Oxide of silicon*,  $\text{SiO}_2$ , or *silica*, as it is called, is, next to the feldspars, the most abundant mineral in the earth's crust, of which, in fact, it forms 12 per cent. In compact, opaque or translucent masses of crystals, silica occurs very abundantly and is, in this form, known as *quartz*. Rock crystal and quartz, however, occur not only in colourless forms but also, owing to the presence of impurities, in various coloured forms, such as amethyst, cairngorm, rose quartz and smoky quartz. Silica occurs also in apparently amorphous but partly crystalline forms—chalcedony, carnelian, chrysoprase, agate, onyx, flint, etc.—

<sup>1</sup> Greek *κρύσταλλος* (*crystallos*), ice.

<sup>2</sup> Derived from Latin *silex*, flint.

and in an amorphous, hydrated form as opal. The waters of the Icelandic geysers, as well also as of those of Yellowstone Park, U.S.A., contain silica in solution, and this is deposited as a compact mass around the mouth of the geyser in the form of mounds, walls or "castles."

Silica is also present in plants—in grasses, bamboo, oats, etc. ; and kieselguhr,<sup>1</sup> which was used by Nobel for the manufacture of dynamite, is composed of the siliceous skeletons of myriads of microscopic water-plants called *diatoms*.

**Quartz Glass.**—When crystalline quartz is heated in the oxy-hydrogen blowpipe flame, or in a specially constructed electric furnace, to a temperature of about 1650° C., it melts to a colourless liquid ; and when this liquid is cooled fairly rapidly, it solidifies to a clear, colourless, glassy mass—a supercooled liquid—which looks just like ordinary glass. It is, however, much more transparent than ordinary glass, not only to the rays of light of the visible spectrum, but also to the ultra-violet rays or invisible rays of short wave-length, now so largely applied in medical treatment. It is, in fact, the most transparent manufactured solid known ; and light may also be transmitted through a bent or curved rod of quartz glass with very little loss. Fused quartz, or quartz glass, possesses also the exceedingly valuable property that it expands and contracts only very slightly with alteration of the temperature (its coefficient of expansion is only 0.00000055, or considerably less than one-tenth that of glass), and for this reason it can, unlike ordinary glass, be rapidly heated or rapidly cooled without cracking. It can, for example, be heated red hot and then plunged into cold water, or when cold, it can be suddenly introduced into the blowpipe flame ; or a wire enclosed within a tube of quartz glass may be heated to a bright red heat by means of an electric current while the tube is immersed in cold water, and the quartz glass remains in all cases uncracked. By reason of this property, quartz glass, formed into apparatus of various kinds and into articles of everyday use (*e.g.* globes for use with incandescent gas mantles), has come increasingly into use in recent years, more especially in cases where rapid changes of temperature are encountered.

Silica, or quartz, is very resistant to acids, except hydrofluoric acid with which it readily reacts, but it is readily dissolved by solutions of alkalis.

When heated for some time to a temperature of about 1150° C., a temperature considerably below the point at which it becomes

<sup>1</sup> That is, in German, siliceous earth.

fluid, the glassy quartz passes into crystalline form; it "devitrifies," and can then no longer withstand, as before, sudden changes of temperature.

**Silicates and Silicic Acid.**—The element silicon, of which silica is the oxide, belongs to the carbon family and is capable of forming compounds analogous to those which are formed by carbon. Its oxide,  $\text{SiO}_2$ , is analogous to carbon dioxide,  $\text{CO}_2$ , and, like this, is an acid oxide which is soluble in and unites with alkalis. The solubility of silica in alkalis was, in fact, known as early as the seventeenth century, and the thick oily liquid obtained by dissolving flint or quartz sand in alkali was called by Glauber *oleum silicium* or *liquor silicium*.

At the present day, *sodium silicate*,  $\text{Na}_2\text{SiO}_3$ , analogous to the compound, sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is produced on a large scale by fusing quartz or white sea-sand (the grains of which consist almost entirely of quartz) with soda. The silica displaces the carbonic acid from the carbonate, and sodium silicate is formed. When the fused mass is allowed to cool, it solidifies to a glassy material which, because of its solubility in water, was, in 1818, given the name of *water-glass*, by the Bavarian chemist, JOHANN NEPOMUK VON FUCHS (1774–1856), who also suggested many of the uses to which it is now put. Commercial water-glass is an aqueous solution of sodium silicate with excess of silica dissolved in it, and it is used as an adhesive for glass or porcelain, as a coating on paper to form washable memorandum tablets, as a preservative for eggs and for numerous other purposes. Its use depends in these and in many other cases on the fact that it readily gelatinises or forms a gelatinous film.

On pouring a dilute solution of water-glass into dilute hydrochloric acid, silicic acid is liberated. As the silicic acid does not

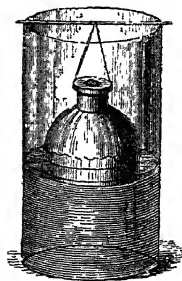


FIG. 77.—Dialyser.

crystallise, it is purified by *dialysis*. The mixture is poured into a vessel known as a *dialyser* (Fig. 77), the bottom of which is formed by a membrane of parchment paper, or into a tube of parchment paper, which is then suspended in water. The sodium chloride formed in the above reaction, as well as the excess of hydrochloric acid, diffuses through the parchment paper into the outside water, whereas the silicic acid does not do so. On concentrating the solution of silicic acid, it sets to a jelly which, on being heated, gradually loses water and finally passes into the oxide,  $\text{SiO}_2$ . The silica so obtained forms a light, white powder. The partially

dehydrated jelly of silicic acid—known as *silica gel*—forms a very porous material and is largely used for the purpose of adsorbing vapours, just as porous charcoal is used for adsorbing gases.

Although the silicates of the alkali metals are soluble in water, the silicates of the other metals, *e.g.* of calcium, magnesium, etc., and compound silicates, such as the *felspars* (*e.g.* potassium aluminium silicate), are insoluble; and many of these form important naturally occurring minerals.

### CLAY

The compound silicates containing an alkali metal, although insoluble in water, are attacked by carbonic acid. When, therefore, felspathic minerals, present so abundantly in granites, are exposed to the prolonged action of atmospheric moisture and carbon dioxide, decomposition takes place with formation of alkali carbonate and aluminium silicate; and this aluminium silicate, in a hydrated state represented by the formula,  $\text{Al}_2\text{H}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ , and known as *kaolinite*, is the main constituent of kaolin or white China clay. To this material is mainly due the plastic properties also of the common clays, in which, however, the aluminium silicate is mixed with varying amounts of quartz, mica, oxide of iron, organic matter, or other impurities.

Clay, the name given to natural deposits of varying composition which become plastic when mixed with water, and which harden on drying, has played a very important part in the development of human civilisation. Even in the early days—perhaps twelve thousand years or more ago—when man was still using implements of flint and stone, he learned that the soft and plastic mud carried down by the rivers, became hard when exposed to the sun, and still more so when heated in the fire; and so he made bricks and built himself a house, and he moulded the clay into rude vessels in which to store his grain or even to cook his food. And as the centuries passed, and the morning of culture broke with the invention of the art of writing, more than five thousand years ago, the Sumerian tribes of the Tigris and Euphrates valleys—one of the earliest centres of civilisation—and the Babylonians, Assyrians and Hittites after them, committed their thoughts and their knowledge to writing on clay;<sup>1</sup> and the library of the Assyrian king, Assur-bani-pal (seventh century B.C.), consisting of 22,000 clay tablets, was the greatest

<sup>1</sup> In Egypt, papyrus was used as the vehicle for writing.

library of antiquity. As time passed, men found in clay a means also of expressing their artistic feeling, and so bequeathed to us beautiful vases of Greek and Etruscan workmanship.

**Porcelain, Stoneware and Earthenware.**—After the fall of the Roman Empire, the potter's art was preserved by the Arabs, and from them it spread to other countries, even to India and China, and in the latter country it attained to great excellence. In due time, during the fifteenth and sixteenth centuries, Chinese porcelain found its way to Europe where, during the seventeenth and eighteenth centuries, it was successfully imitated; and from that time, the manufacture of porcelain has developed greatly in all the countries of the West.

In the manufacture of porcelain, the purest china clay together with the requisite amount of ground felspar and quartz is made into a "slurry" or suspension in water, and then passed through filter presses. In this way is obtained a soft plastic mass which after being formed on the potter's wheel or in a mould is heated in a kiln to a high temperature ( $1200^{\circ}$ – $1300^{\circ}$  C.). In this process, the clay loses water and passes into the anhydrous silicate  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and the felspar fuses and dissolves part of the quartz. A glass is thus produced which binds the mass together and renders it non-porous and non-absorbent of water. The mass also becomes translucent, in proportion to the amount of glassy material formed.

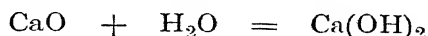
In the production of stoneware, less pure materials are used and the fusion of the felspar is not so complete. The body of the ware, therefore, although non-absorbent, is not translucent.

In the manufacture of earthenware, the temperature at which the ware is fired is lower than in the case of stoneware, so that very little vitreous material is formed, and the body is porous. This is called "bisque" or "biscuit." When pure materials are used, a white earthenware, invented by the English potter, JOSIAH WEDGWOOD (1730–1795), and used as table-ware, is obtained.

After the ware has been fired, it is coated with fusible material, such as ground felspar, lead borosilicate, etc., and again heated to a temperature of about  $1000^{\circ}$  C. A glassy film or glaze is thereby formed on the surface of the ware. For cheap earthenware, a *salt glaze* may be used. This is obtained by throwing salt into the firing kiln, when the vapour reacts with the clay forming a fusible sodium aluminium silicate which coats the ware with a glaze.

Colour decoration, by means of coloured oxides, may be applied to the ware before glazing, or in the form of fusible enamels after glazing. The colours are then fixed by re-firing.

**Mortar and Cement.**—In the far-off days when man first began to build with sun-dried bricks, he used as his binding material, moist clay, which hardened on drying; but at a much later date when the kings of Egypt erected the pyramids of stone, they used a cement obtained by heating gypsum—a cement now known as plaster of Paris. The formation of plaster of Paris by heating gypsum doubtless led to the discovery of ordinary mortar. Limestone or calcium carbonate, when strongly heated, decomposes, as has been pointed out, into *quicklime* (calcium oxide) and carbon dioxide; and when water is added to quicklime, combination takes place with evolution of heat and production of *slaked lime* or calcium hydroxide:



In the making of mortar, the slaked lime is mixed with a certain amount of sand, to prevent too great a contraction taking place when the mortar sets; and the setting of the mortar depends on the fact that, on drying, the slaked lime forms a quasi-gelatinous material which binds the bricks or stones, and also that, when it is exposed to the air, it reacts with the carbon dioxide to form calcium carbonate.

Useful as lime mortar is for structures on dry land, it will not “set” when in contact with water; but even in early Roman times, as the architect VIRUVIUS, writing in the first century B.C., states,<sup>1</sup> it was known that “there is also a kind of powder which from natural causes produces astonishing results. It is found in the neighbourhood of Baiæ and in the country belonging to the towns around Mount Vesuvius. This substance, when mixed with lime and rubble, not only lends strength to the structures of other kinds, but even when piers are built of it in the sea, they set hard under water.” This naturally occurring material, known in later times as *pozzuolana* (a siliceous tufa of volcanic origin), gives rise to calcium silicate when mixed with slaked lime and water, and was long used by the Romans as a hydraulic cement. Ground blast-furnace slag, which contains lime, alumina and silica in combination, acts similarly when mixed with lime.

With the decline of Roman power, the knowledge of cements was lost, and it was not till 1756, when the English engineer, JOHN SMEATON, was engaged in the work of building the Eddystone lighthouse in the English Channel, that the method of producing a hydraulic cement by mixing a burned argillaceous

<sup>1</sup> Marcus Vitruvius Pollio: *de architectura*, Book II, Chap. 6. Translated by M. H. Morgan.

limestone with pozzuolana, was rediscovered. Owing to the scarcity of pozzuolana, however, attempts were made to obtain a cement without its use, and in 1824-25, the efforts of the English bricklayer, JOSEPH ASPDIN, of Leeds, were crowned with success. The cement which he obtained he called *Portland cement*, on account of its resemblance to a well-known building stone, Portland stone.

The raw materials used are generally clay and limestone or other form of calcium carbonate.<sup>1</sup> These are mixed together so as to give the proper proportions of lime, alumina and silica, ground to a fine powder and heated to the point of incipient fusion in rotary kilns. These cylindrical kilns, built up of steel plates and lined with firebrick, are five to ten feet in diameter, and from one hundred to two hundred and fifty feet in length. The kiln is slowly rotated and the raw material passes down the tube to regions of higher and higher temperature produced by a flame of pulverised coal or fuel oil. The partially fused mass which is thus obtained is ground to a fine powder and constitutes the Portland cement of commerce.

*Concrete*, now so largely employed for building purposes and for road making, is a mixture of Portland cement with sand or gravel.

Portland cement is a mixture more especially of silicates of calcium (*e.g.* the silicate,  $3\text{CaO}, \text{SiO}_2$ ) and calcium aluminate ( $3\text{CaO}, \text{Al}_2\text{O}_3$ ), which have been formed by the interaction of the raw materials at the high temperature of the kiln. Of the different constituents, the most important as a cementing material appears to be the calcium silicate, the cementing value of which is due to the readiness with which it gives rise to a gelatinous silica when mixed with water.

### CALCIUM CARBONATE

Calcium carbonate, or carbonate of lime, which, as we have just seen, is used so largely in the manufacture of Portland cement, occurs very abundantly and widely distributed, in various forms. *Chalk* and *limestone* have been formed from the shells or skeletons of marine organisms, deposits of which have become compacted under pressure; and *coral* is built up by the minute coral polyp. *Marble* is a limestone which has been transformed by heat and pressure into a mass of small crystals. Large

<sup>1</sup> At Redwood City, California, the raw materials, consisting of a mixture of an argillaceous mud and oyster shells (calcium carbonate), are dredged from the bottom of San Francisco Bay.



transparent crystals of calcium carbonate are also found as *calcite* or *Iceland spar*. This material has the property of double refraction, so that an object appears double when viewed through a crystal of Iceland spar (Fig. 78). *Pearls*, also, consist essentially of calcium carbonate deposited by the oyster, layer on layer, on a particle of some foreign body.

Although calcium carbonate is sparingly soluble in pure water, it is, as has already been pointed out, converted into the soluble *calcium bicarbonate*,  $\text{Ca}(\text{HCO}_3)_2$ , by water containing carbon dioxide in solution. This fact is one of great economic and geological importance. Not only is this solvent action

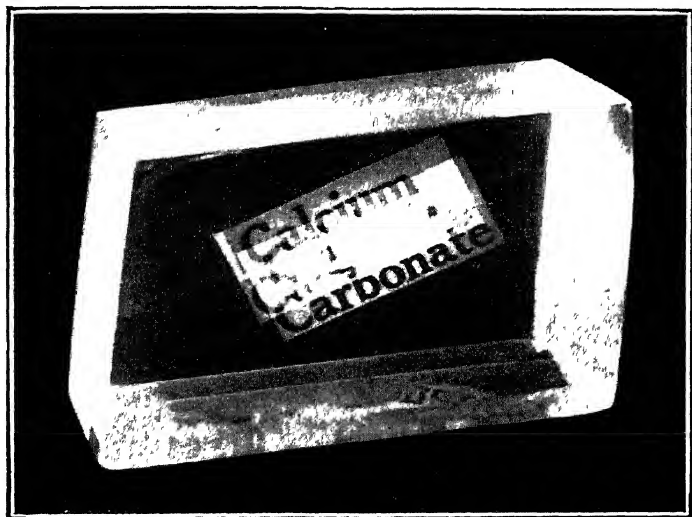


FIG. 78.—Iceland spar, showing double refraction

responsible for the production of the hard water which is met with in all limestone or chalk districts, but it is the chief agent by which lime is transported through the soil and rendered available for plants.

How great is the solvent action of carbonic acid, acting through the ages, is seen from the great limestone caves, like the Mammoth Cave, Kentucky, which has been gradually eaten out of the solid rock by water containing carbonic acid. No sooner, however, are these caves formed than Nature begins to fill them up again; for the rain water, percolating through and dissolving the rock, evaporates and leaves behind a minute grain of limestone. As drop follows drop through endless years, grain

is added to grain, and an icicle-like *stalactite* hangs pendent from the roof. As Shelley has so beautifully written :<sup>1</sup>

From the curved roof the mountain's frozen tears,  
Like snow or silver or long diamond spires,  
Hang downward, raining forth a doubtful light.

If the drops of water come faster, some may fall to the floor of the cave, and, evaporating there, build up a mighty column or *stalagmite*. Many and varied, graceful and grotesque,



(Courtesy Union Pacific System.)

(Copyright J. E. Haynes, St. Paul.)

Limestone Terraces, Mammoth Hot Springs, Yellowstone Park.

delicate and massive, are the forms which may thus be produced, and the sight presented by such a cave, suitably illuminated, is one of the most impressive that can be experienced.

Spring water carrying calcium bicarbonate in solution will deposit calcium carbonate as the carbon dioxide escapes and the water evaporates. In this way there have been and are being formed, for example, the great terraced basins of limestone deposited from the water at Mammoth Hot Springs, Yellowstone Park, U.S.A. Wood, also, impregnated with such water, becomes petrified through incrustation with carbonate of lime.

<sup>1</sup> *Prometheus Unbound*.

## GLASS

Important as has been the part played by clay in the history of human civilisation, a part of even greater importance has been played by that other siliceous material, glass.

Many, doubtless, are familiar with the legend reported by the Roman writer PLINY in the first century of our era, which ascribed the discovery of glass to a party of Phœnician sailors who were forced by stress of weather to land on the sandy shore under Mount Carmel. Here, standing their cooking-pots on lumps of soda, with which their ship was laden, they observed the soda and the sand to fuse together under the heat of the fire, and so to form a glass.

Although it may be that it was by some such accident that glass was discovered,<sup>1</sup> and although the Phœnician towns of Tyre and Sidon were, at an early period, almost as celebrated for their glass as for the famous purple dye which coloured the robes of kings, it is to Egypt that we must look for the first knowledge of glass or glass-like material; to that country which, as Herodotus wrote, "contains more wonders than any other land, and is pre-eminent above all other countries of the world for works which almost baffle description."

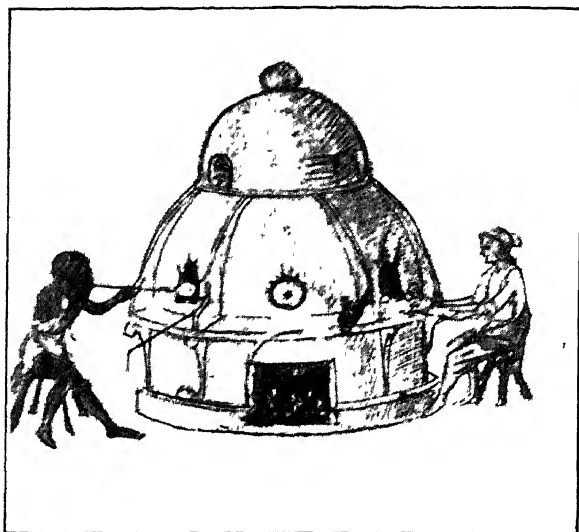
Even in pre-dynastic times (before 3000 B.C.), the Egyptians had discovered how to produce a glazed faience; and from this glaze, glass was evolved as an independent material about the sixteenth century B.C. At first, glass was opaque and coloured by impurities, and used for beads and ornamental purposes. The use of glass for windows was introduced by the Romans, but it was a great luxury which only the wealthy could afford; and although, as early as the seventh century, the windows of the great cathedrals were glazed, most private houses and smaller churches had to be content with paper, bladder, mica, etc. In the words of the French proverb: "*L'abbaye est pauvre, les vitres ne sont que de papier.*"

What mankind owes to the first discoverer of the process of making clear and colourless glass, it is scarcely possible to describe. That first artificer in glass, as Dr. Johnson wrote, "was facilitating and prolonging the enjoyment of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures; he was enabling the student to contemplate nature and the beauty to behold herself." And in recent years glass has undergone a wonderful evolution through the work and

<sup>1</sup> The sand of Egypt contained lime, and such sand when fused with soda would yield an insoluble glass.

labours of chemists, who have shown how, by variation of the composition, the properties of glass may be altered in a most marvellous degree; and they have thereby made possible the construction of apparatus for the most diverse uses—prisms and lenses for lighthouses, microscopes, telescopes and other instruments—and so have contributed to the service of man and a knowledge of the universe.

Unlike fused quartz or silica glass, ordinary glass is not a single substance, but a homogeneous mixture of silicates in which the silicate of sodium or of potassium is always present. Glass has, therefore, no definite composition, and by varying



Mediæval glass furnace.

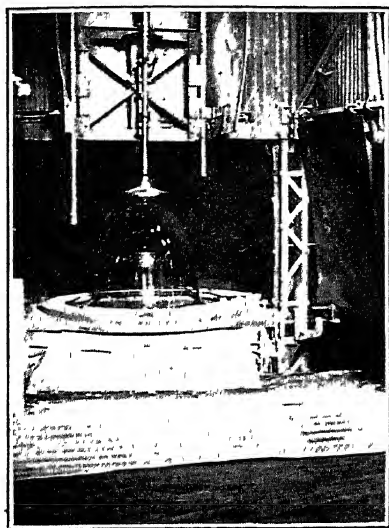
not only the constituents but also their relative amounts, glasses of various kinds and possessing very different properties can be obtained.

Ordinary window glass and glass for table-ware and for general use, consist essentially of a mixture of the silicates of sodium and of calcium, although aluminium silicate is also present in very small amount. The quality and appearance of the glass depend largely on the purity of the materials employed in its manufacture.

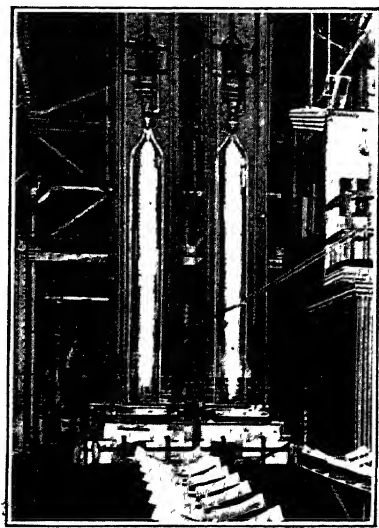
Fine quartz sand, sodium carbonate and sulphate,<sup>1</sup> and white chalk or limestone, are thoroughly mixed together in the proper

<sup>1</sup> Research has shown that the addition of sodium sulphate, as also of small quantities of aluminium silicate, has the effect of strengthening the finished glass.

proportions, and the mixture is melted in large fire-clay pots, or in large rectangular tanks, placed in furnaces which are now generally heated by means of gas. At first the molten mass is almost opaque owing to the multitude of bubbles of carbonic acid gas which permeate it, but after a time these bubbles escape, and a clear liquid is obtained. The desired article can then be formed either by pouring the molten glass into moulds or by blowing. In the latter case, a quantity of molten glass is taken up on the end of a long metal tube, and by blowing through the tube, hollow articles of varied shape can, by the expert skill of



A



B

(Courtesy Prof. A. Silverman.)

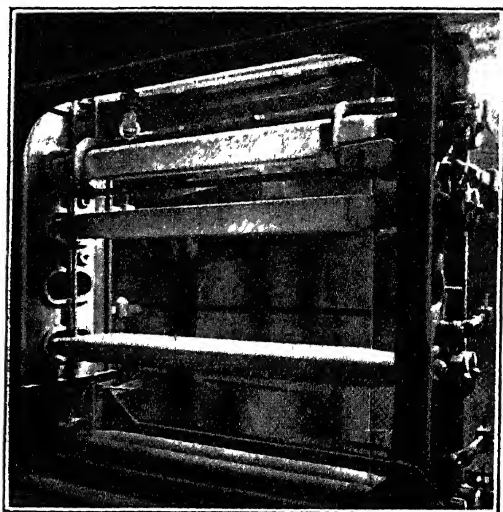
Cylinders of glass produced by the Lubbers process.

A, cylinder being formed; B, finished cylinders.

the glass blower, be obtained. For the production of "sheet glass," used for windows, various processes are employed.

In one process, glass cylinders are first blown by a method invented by J. H. LUBBERS in 1896. A metal plate, shaped like an inverted saucer but with inturned edges, is lowered just below the surface of a mass of molten glass. Through a tube in the middle of the plate, air is now forced and a bubble, about two feet in diameter, is formed on the surface of the liquid. Very slowly, so that the motion is just perceptible, the metal plate is drawn upwards. The bubble is thus slowly raised, and as it rises it draws the viscous molten glass with it, and this,

solidifying as it leaves the surface of the bath, forms a cylinder. A slight pressure of air is maintained inside the cylinder so as to keep the walls from collapsing. In this way, very slowly, a cylinder about two feet in diameter and perhaps forty feet in height is gradually formed. This is then cracked off at the bottom, lowered on to a horizontal support and cut into suitable lengths by means of an electrically heated wire. These short cylinders are then cracked lengthwise by means of a hot rod and placed in an oven heated to the softening point of the glass. The cylinder begins to unroll, and is then flattened out into a sheet by means of a special instrument.



Sheet glass produced by the Fourcault process passing between rollers.

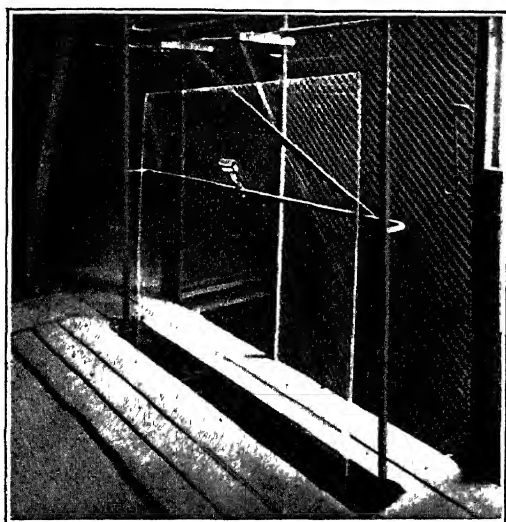
(From *Glustechnische Berichte*, 1928.)

By another process, developed more especially in Belgium by EMILE FOURCAULT and in America by IRVING W. COLBURN, sheet glass is produced by lowering a metal bar into the molten glass. As the bar is raised the glass adheres to it and solidifies, and in this way a sheet of glass can be drawn in much the same way as the cylinder of glass in the Lubbers process. The sheet of glass is drawn slowly upwards between asbestos-covered rollers enclosed in a tall metal box, and is thus slowly cooled. As it passes out at the top of the box, it can be cut into lengths as desired.

The surface of this glass is not quite plane, but is covered

with slight depressions and ridges, and in consequence of this, objects viewed through such glass are more or less distorted. To get rid of this defect, the sheet glass is sometimes ground and polished, as in the case of plate glass, and in this way one obtains what is known as "patent plate." Such glass is largely used for the framing of pictures.

Glass articles which have been formed by blowing or moulding, must be again heated to near the softening point and then placed in an "annealing" chamber, where they can cool very slowly. The purpose of this is to get rid of the stresses which are set up in the rapidly cooled glass and which render the glass very



Sheet glass produced by the Fourcault process. Glass at top of cooling chamber ready to be cut.

(From *Glastechnische Berichte*, 1928.)

liable to fall to pieces when scratched. This can be illustrated by what are known as "Rupert's drops," obtained by dropping molten glass into hot oil, so that the glass is suddenly cooled. This glass is very hard, and can withstand even heavy blows with a hammer, but if the "tail" attached to the drop is broken, or if the glass be scratched with a file, the whole drop falls to a powder.

That glass can be toughened or hardened by cooling rapidly in oil or otherwise, appears to have been known at least as early as the first century A.D., as the following incident, related by Petronius in that excellent satire, *Cena Trimalchionis*, shows :

“ There was an artist who made glass vessels so tough and hard that they were no more to be broken than gold and silver ones. It so happen'd that the same person having made a very fine glass mug, fit for no man, as he thought, less than Cæsar himself, he went with his present to the Emperor, and had admittance ; both the gift and the hand of the workman were commended, and the design of the giver accepted. This artist, that he might turn the admiration of the beholders into astonishment, and work himself the more into the Emperor's favour, begged the glass out of Cæsar's hand ; and having received it, threw it with such a force against a paved floor, that the most solid and most firmest metal could not but have received some hurt thereby Cæsar also was equally amazed and troubled at the action ; but the other took up the mug from the ground, not broken but only a little bulg'd, as if the substance of metal had put on the likeness of glass ; and therewith taking a hammer out of his pocket he hammer'd it as if it had been a brass kettle, and beat out the bruise : and now the fellow thought himself in heaven, in having, as he fancied, gotten the acquaintance of Cæsar, and the admiration of all mankind ; but it fell out quite contrary to his expectation : Cæsar asking him if anyone knew how to make this malleable glass but himself, and he answering in the negative, the Emperor commanded his head to be cut off ; ‘ For,’ said he, ‘ if this art were once known, gold and silver will be of no more esteem than dirt.’ ” In such fashion did Nero encourage and foster science.

By a systematic study of the influence of a large number of substances on the properties of glass, hundreds of different glasses have been produced and their physical and optical properties examined. Some of these glasses have proved themselves to be of the highest value, and have made possible the construction of apparatus and instruments by which scientific knowledge and material well-being have been greatly promoted. Moreover, glasses possessing very different expansibilities with heat have also been produced, and by welding together combinations of these, glasses have been obtained which undergo little change of volume on heating and can withstand even considerable and sudden alterations of temperature without cracking.

In recent years heat-resisting glass with low coefficient of expansion has come into use for cooking utensils (*e.g.* pyrex ware). Such glass is obtained by reducing the proportion of soda and increasing the proportion of silica. Pyrex glass contains 80 per cent. of silica, 12 per cent. of boric oxide, with smaller amounts of soda and alumina (aluminium oxide). The value of



glass as compared with metal ware for cooking purposes depends on the fact that glass reflects a comparatively very small proportion of the radiant heat which reaches it, so that baking takes place more rapidly in glass than in metal dishes.

The green colour so well known in the case of cheap bottle glass, and seen in practically all old window glass, is due to the presence of small amounts of iron oxide derived from the impure materials, especially the sand, used in the manufacture of the glass. This green colour can be "corrected" by the addition of black oxide of manganese. The amethyst colour which is thereby produced neutralises the green due to the iron, and a white glass is obtained. The amethyst or purple colour due to the manganese becomes evident when such glass is exposed for a lengthened period to bright sunlight.

By fusing silica with a mixture of potash and red lead (oxide of lead), a lustrous glass with a high refractivity is obtained, and is known as "crystal." When cast in suitable moulds, or, preferably, cut with a wheel and polished, it is much prized for vases and ornamental dishes of different kinds. A still more lustrous glass can be obtained by replacing part of the silica in the crystal glass mixture by boric acid, and so giving rise to what is called generally a boro-silicate glass. By reason of its brilliant lustre and high refractive power, such a glass, when suitably cut, sparkles and flashes in a myriad colours. It is, therefore, largely employed under the name of "strass," or "paste," for counterfeiting diamonds, and, when suitably coloured, other gems as well.

When glass is heated for some time to a temperature just below the softening point, it *devitrifies* and becomes opaque, owing to the crystallisation of the silicates present in the glass.

The production of coloured or stained glass is easily effected by adding small quantities of suitable substances to the molten mixture of silicates. Thus, as has already been mentioned, addition of iron imparts a green colour to the glass, whereas the addition of manganese oxide imparts to the glass an amethyst or purple shade. Salts of the metal uranium give to glass a yellowish-green fluorescence, and are much used in the production of fancy glass. With cobalt oxide the colour is deep blue, while with gold, a ruby red is obtained. Paste, coloured blue with cobalt, or red with gold, is used to counterfeit the sapphire and the ruby. These counterfeit gems must not be confused with the artificially prepared sapphires and rubies to which reference was made previously (p. 315). They can readily be distinguished

from the latter or from the naturally occurring gems by their much greater softness.

In most cases the colour in glass is due to the formation of coloured silicates, *e.g.* silicate of manganese, silicate of cobalt, etc.; but in the case of ruby glass, the colour is due to the presence of excessively minute particles of metallic gold. When a small quantity of gold is added to molten glass it dissolves, much as sugar dissolves in water, and if the glass is rapidly cooled it is found to be white or to have only a very faint yellow tinge. If, however, this glass is reheated, or if the molten glass is allowed to cool very slowly, metallic gold begins to be formed in very minute particles. As the particles increase in size, the colour deepens more and more to a dark ruby red, and different shades can be obtained by careful regulation of the heating and cooling. The particles, however, are so minute that they are quite invisible not only to the naked eye, but even under a powerful microscope, and the gold is said to be in the *colloidal* state—a state of matter which will be discussed in the following chapter. If too much gold is added, the metal may separate out in visible particles and so render the glass opaque. If selenium is added to a glass in which the place of lime has been taken by zinc oxide, a highly transparent red glass, much used for signal lamps, tail-lights of automobiles, etc., is obtained.

Glass is also used in large quantities for the production of mirrors, which are greatly superior to the polished metal mirrors of our forefathers. In order to avoid distortion, plate glass, the surface of which has been polished quite plane and smooth, must be used, and one side of this is “silvered.” Formerly, this was effected by coating the glass with an amalgam of tin and mercury, but mercury is a very expensive metal, and its use also involves the danger to the workman of mercurial poisoning. For the production of mirrors, therefore, this metal has been superseded by silver, the use of which is not only free from danger but allows also of a whiter reflecting surface being obtained. By adding caustic soda and ammonia to the solution of a silver salt, *e.g.* silver nitrate, a solution of silver oxide is obtained from which metallic silver can readily be caused to separate out by the addition of certain reducing substances, such as glucose. The surface of the mirror glass, previously well cleaned, is laid on the silver solution, and if the conditions are properly arranged, the silver separates out very slowly and forms a coherent and highly reflecting coating on the surface of the glass.

## CHAPTER XXV

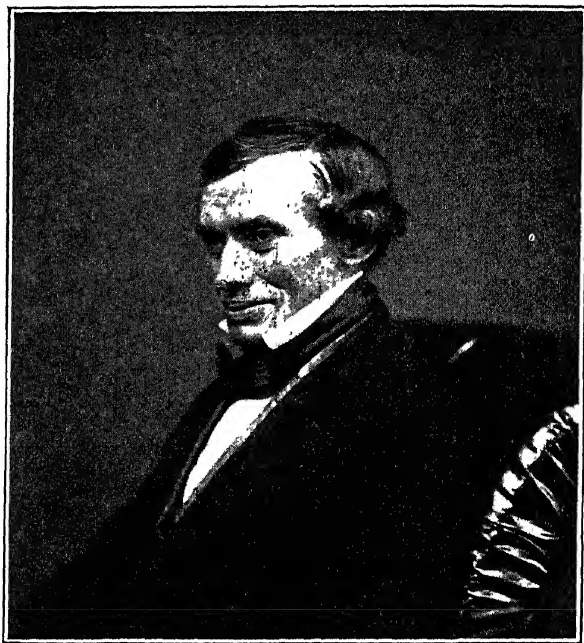
### THE COLLOIDAL STATE

WHEN the ordinary coarse matter which we can see and handle is crushed and ground, it can be broken up into smaller and smaller particles. At first, the separate particles may still be seen by the unaided eye, but as the process of grinding is continued, the particles become so small that they can be distinguished only with the help of a lens or of a microscope. One can, in imagination at least, and to some extent also in actual practice, carry the process of subdivision still farther, so that the particles become too small to be seen even with the aid of the most powerful microscope: and the process of subdivision may be continued until, at length, one reaches the ultimate limit or degree of subdivision, the molecule, beyond which farther subdivision is impossible without destroying the chemical nature of the substance. Since the smallest particle of matter directly visible under the microscope is, perhaps, about a thousand times larger than the simplest molecule, there exists, as one can readily understand, a considerable range of subdivision of matter between the limits of the microscopically visible and the molecular state; and it is to this intermediate zone of subdivision of matter—this twilight zone of matter, as one may call it—that the term “colloidal state” of matter is applied.

It may, perhaps, seem strange that this particular range of subdivision of matter should be singled out for special consideration, but the justification for this is found in the fact that matter in the colloidal state possesses properties which are not exhibited, or are not exhibited so markedly, either by molecular matter or by the grosser microscopic particles. Moreover, not only does matter in the colloidal state of subdivision present many problems of peculiar fascination to the student of natural phenomena, but it plays also a very important part in the most diverse fields—in almost every field one may say—of human activity. In agriculture and in the tanning of leather; in the working of clay for the manufacture of the common brick or for

the production of the finest porcelain; in the production of artificial silk and of smokeless ammunition; in the dyeing of textile fibres and in the production of the blue of the sky or the blue of the eye, the colloidal state of matter plays a part. When, further, it is recalled that Nature has selected matter in the colloidal state to be the vehicle of life and as the medium in which all life processes take place, the importance and interest of a study and knowledge of the colloidal state become obvious.

It is to the Scottish chemist, THOMAS GRAHAM (1805-1869),



THOMAS GRAHAM.

the discoverer of the law of diffusion of gases, that one usually assigns the credit of inaugurating the investigation of the colloidal state of matter. This position of honour in the history of scientific development was achieved, not so much by a profound contribution to our knowledge of the properties of the colloidal state, as by his discovery of a useful and convenient method of distinguishing between the molecular state of subdivision in which a substance exists in true solution, and the state of subdivision known as colloidal. As a result of his investigation of the diffusion of dissolved substances through

parchment paper or animal membrane, Graham, in 1861, found that while certain substances in solution pass through such a membrane, other substances do not do so. Since the substances, salt, sugar, etc., which could pass through the membrane were such as generally crystallise well, whereas those which did not pass through, *e.g.* gelatin, starch, silicic acid, etc., were believed to be amorphous and non-crystallisable, Graham divided substances into two classes, *crystalloïds* and *colloids*,<sup>1</sup> and this distinction was long maintained. Although it is now recognised that the distinction between crystalloids and colloids is to be found in the degree of dispersion or subdivision, yet from the practical point of view Graham's classification is of importance; for the process of *dialysis* discovered by Graham, gives a means, still generally employed, of separating and distinguishing between molecularly dispersed matter, existing in true solutions, and matter in the colloidal state of subdivision. By this means, substances in the colloidal state, *e.g.* silicic acid, can be obtained free from crystalloids, or substances which exist molecularly dispersed in solution. The smaller particles, the molecules, can pass through the membrane, the larger particles cannot.

The difference in diffusibility of molecules and colloidal particles is clearly demonstrated by the following simple experiment. Into two test-tubes is poured a 3 per cent. solution of gelatin, so as to form a layer about two inches in depth. After the gelatin solution has set to a jelly, there is poured into one of the tubes, a deep-blue coloured solution obtained by adding ammonia solution to a solution of copper sulphate; and into the other tube, a deep-blue coloured colloidal sol of Prussian blue, obtained by adding a dilute solution of ferric chloride to a dilute solution of potassium ferrocyanide. After a few hours, it will be found that the blue copper compound has penetrated some distance into the gelatin layer, whereas the colloidal Prussian blue has not penetrated into the gelatin layer at all.

Although Graham and many others after him were concerned mainly with finely subdivided solids dispersed in a liquid medium, it must be recognised that colloiddally dispersed matter may exist in the solid, liquid or gaseous state, and that the dispersion medium also may be solid, liquid or gaseous, as in colloidal suspensions, emulsions, smokes, mists, etc. We shall confine the discussion here to those systems in which water is the dispersion medium.

**Heterogeneity of Colloidal Sols.**—While it could be inferred from the experiments of Graham that the apparently homo-

<sup>1</sup> From the Greek *κόλλα* (*kolla*), glue.

geneous colloidal solutions, or colloidal *sols* as they are called, in order to distinguish them from true solutions, are in reality heterogeneous and contain particles which have a magnitude greater than molecular, the existence of such particles is rendered evident to the eye by means of the *Tyndall Phenomenon*.

If sunlight be allowed to pass through a hole in the shutters of a darkened room, the path of the beam is made evident by a diffused light in which the larger dust particles are seen to

“ Glitter like a swarm of fire-flies, tangled in a silver braid.”

This diffused light is due to the presence of particles which are large enough to reflect and scatter the waves of light, although too small to be seen as separate individuals by the eye. So also, by means of this “ Tyndall phenomenon,” as it is called, the presence of particles in a colloidal sol can be detected. If a beam of light is passed through pure water or through a solution of salt, the path of the beam is invisible ; the liquid is “ optically empty.”<sup>1</sup> But if the beam is passed through a colloidal sol, the path of the beam is traced by a diffused light, like the sun-beam in a darkened room.

By means of the Tyndall phenomenon, then, one can detect the presence of particles too small to be seen in the ordinary way, if only the light reflected or dispersed by the particles, and not the direct rays from the source of light, are allowed to enter the eye. And it will be clear that if, instead of the unaided eye, one employs a microscope to examine the scattered light, the range of vision will be extended, and it will be possible to detect, although not actually to see in their own shape and colour, particles which are much smaller than can be seen when the microscope is used in the ordinary way. On the basis of this principle there has been devised an arrangement known as the *ultra-microscope*, by means of which not only the heterogeneity of colloid sols can be detected, but also the number of particles in a given volume of the sol determined. The arrangement is shown diagrammatically in Fig. 79. A powerful beam of light is sent horizontally into the liquid under investigation at right angles to the line of vision through the microscope. If the liquid under examination is optically empty, the field of view in the microscope will appear quite dark ; but if particles are present in the liquid, the light will be reflected and dispersed, and the minute points of light thus produced will stand out as bright

<sup>1</sup> Owing to the presence of floating particles even in filtered water, the “ Tyndall phenomenon ” will be observed with ordinary pure water. Special precautions must be adopted to free the water from all suspended particles.

specks against a dark background, in the field of view of the microscope.

A very suitable liquid for examination with the ultra-microscope is colloidal gold sol which formed the basis of the "potable gold" of the alchemists, and was rediscovered in 1856 by FARADAY, who obtained it by the reduction of gold chloride with phosphorus. The sol can readily be prepared by adding to a very dilute neutral solution of gold chloride a dilute solution of tannin (tannic acid). In the cold, no change occurs, but when the liquid is heated a pink colour soon begins to develop; and by making further additions of the gold and tannin solutions, a clear deep ruby-red coloured liquid is obtained. This contains

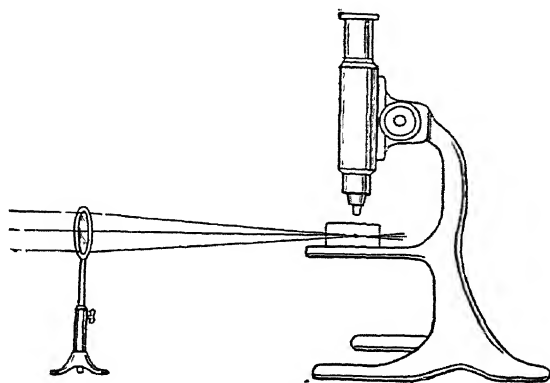


FIG. 79.—Ultra-microscope.

the gold in a colloidal state, and is similar, in fact, to ruby glass (p. 398).

On account of their smallness, these ultra-microscopic, colloidal particles exhibit the phenomenon of Brownian movement with extraordinary vividness. As RICHARD ZSIGMONDY, Professor of Physical Chemistry in the University of Göttingen, wrote: "A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold. They hop, dance, spring, dash together and fly apart so rapidly that the eye can scarcely make out their movements."

And how large are those particles which are thus detected in the apparently homogeneous sols? With the aid of even the most powerful microscope, the smallest particle that can be seen by the ordinary method must have a diameter of not less than about  $\frac{1}{10000}$ th part of a millimetre or  $0.1\mu$ ; <sup>1</sup> but by means of

<sup>1</sup> A *micron*, represented by  $\mu$  (Greek *mu*), is equal to one-thousandth of a millimetre (0.001 mm.), and a *millimicron*, represented by  $\mu\mu$ , is equal to one-thousandth of a micron, or equal to one-millionth of a millimetre.

the ultra-microscope, particles having a diameter of less than six-millionths of a millimetre ( $1000000$  mm.), or 6 millimicrons ( $6\mu\mu$ ), can be detected.

Some idea of the dimensions of the colloidal particles will be obtained from the statement that the diameter of the human red blood corpuscles is about  $7.5\mu$ , micrococci have diameters of the order  $1\mu$ , while the particles of colloidal gold sol have diameters of  $7-15\mu\mu$ . The molecule of hydrogen has a diameter of about  $0.1\mu\mu$ , that of sodium chloride a diameter of about  $0.26\mu\mu$ , and that of cane sugar a diameter of about  $0.7\mu\mu$ , or about one-tenth of the dimensions of the smallest particles detectible by means of the ultra-microscope. The colloidal state, then, may be said to refer to matter in a state of subdivision lying between  $0.1\mu$  and  $1\mu\mu$ .

From the investigations carried out by means of the ultra-microscope, it is found that colloidal sols may contain particles of very different size, even in the case of the same substance, and there is every reason to believe that there exist, in some at least of the sols, particles which are smaller than can be detected by the ultra-microscope, although they are of greater than molecular dimensions. In short, there appears to be no sharp division between colloidal sols and true solutions, and it is possible to pass gradually and without break from one to the other.

With regard to the dispersion of light by very small colloid particles, it may be mentioned that the shorter waves of light—the blue of the spectrum—are scattered more than the longer waves which make up red light. Consequently, when the path of a beam of light is observed from the side, against a dark background, the scattered light waves which enter the eye are mainly the shorter wave-lengths, and so the sensation of blue is obtained. If, however, the colloiddally dispersed matter is viewed by transmitted light, the colour appears red. The very fine smoke rising from a wood fire, for example, appears of a blue colour when it is illuminated from the side and when it is viewed against a dark background; but when one views the smoke against a background of white clouds—that is, by transmitted light—the smoke appears reddish-brown in colour.

In the same way, as LEONARDO DA VINCI (1452–1519) suggested long ago, one may explain the blueness of the sky by the scattering of the sunlight by finely dispersed particles in the atmosphere (or, as is now thought, by the molecules of the atmospheric gases themselves), the background being the blackness of infinite space. The blue colour of the iris of the eye and the blue colour of feathers are similarly to be explained—as WILDER D. BAN-



CROFT, of Cornell University, has so fully shown—as due to the scattering of light by finely dispersed matter.

**Adsorption.**—Since matter in the colloidal state is very finely subdivided, the extent of surface exposed is very large relatively to the total volume of the matter.<sup>1</sup> Surface forces, therefore, play a predominant part and bring about changes in the distribution or concentration of matter at the surface of the particles. This change of concentration at a surface, brought about by surface forces, is spoken of as *adsorption*, and has many important applications. It is, for example, in the phenomenon of adsorption that one finds the explanation of the property of charcoal of removing noxious and obnoxious gases from the air, and of colouring matter from solution. The use of porous silica gel for the recovery of volatile solvents, the removal of gasoline vapour from natural gas, and of sulphur compounds from crude petroleum, likewise depends on the very large surface exposed by the gel and its consequently great adsorptive power.

In the production and characterisation of colloidal systems, adsorption plays a very important part. By the adsorption of ions from the dispersion medium or from electrolytes present in solution, the colloid particles acquire an electric charge; and adsorption of the dispersion medium as a whole may also take place to a greater or less extent. Thereby, variation in the general behaviour of colloids may be produced. In the case of the so-called *suspensoid* or *hydrophobe*<sup>2</sup> colloids, such as colloidal sols of gold or of arsenious sulphide, the dispersed particles adsorb none or practically none of the dispersion medium; and they exist therefore in suspension as non-hydrated particles, the stability of which is due to their Brownian movement and, more especially, to the electric charge which they carry. In the case of the so-called *emulsoid* or *hydrophile* (or, generally, *lyophile*) colloids, such as colloidal sols of gelatin or silicic acid, the dispersion medium itself is adsorbed, to a greater or less extent, and the stability and properties of such a colloidal sol are due to the adsorbed water as well as to the electric charge on the particles. The greater the adsorption of the dispersion medium, the more will the stability and properties of the colloidal sol be dependent on this adsorbed medium, and the less will they depend on the electric charge.

The existence of an electric charge on the colloidal particles

<sup>1</sup> If a cube of 1 cm. side were subdivided into cubes with a side of one-millionth of a millimetre, the total surface would be increased from 6 square cm. to sixty million square centimetres or 6000 square metres.

<sup>2</sup> That is, "water-hating." As a general term one uses *lyophobe* or "solvent-hating."

can conveniently be demonstrated with a colloidal sol of sulphide of arsenic ( $\text{As}_2\text{S}_3$ ), which can readily be obtained by passing sulphuretted hydrogen into a solution of white arsenic (arsenious oxide). If the colloidal sol is placed in a U-shaped tube, and if wires connected with the terminals of a high voltage battery or dynamo (the ordinary electric-lighting circuit can conveniently be employed), are inserted in the liquid, one in either limb of the tube, it will be found that the sulphide of arsenic migrates towards and collects around the positive terminal. The particles of arsenic sulphide, therefore, carry a negative charge of electricity. Even with fine suspensions, such as a suspension of fine clay, the same phenomenon is observed; the clay particles collect around the positive terminal in a firm mass. Since the effect depends primarily on the voltage of the current, while only an insignificant amount of electricity is used, this process of *cataphoresis*,<sup>1</sup> or electric transport of suspended particles, constitutes a very economical means of freeing a fine suspension from water; and it has, in fact, been applied to the drying and purification of clay.

The process of cataphoresis or electrophoresis is also applied to the manufacture of articles of rubber. The juice or latex of the rubber plant consists of a liquid in which negatively charged colloidal particles of rubber are suspended, and these particles will therefore be carried to the positively charged electrode or anode. Moulds of any desired form, or fabric or wire, may thus be coated with a layer of rubber, and in this way hot-water bottles, bathing caps, etc., may be produced, or wire may be insulated.

**Precipitation of Suspensoids.**—Since the stability of suspensoid or hydrophobe colloids is mainly due to the electric charge carried by the particles and their consequent mutual repulsion, precipitation of the colloid is brought about by neutralising the electric charge. This can be readily effected by the addition of an electrolyte which, as we have seen, gives rise in solution to positively and negatively charged ions. Negatively charged colloid particles will preferentially adsorb the positive ions of the added electrolyte, and positively charged colloids the negative ions, the charge on the colloid being thereby more or less completely neutralised. When the electric charge on the colloid is neutralised, agglomeration of the particles, followed by precipitation, takes place, the colloidal precipitate so produced being known as a *gel*. Thus, if a small quantity of hydrochloric acid (hydrogen ion) or calcium chloride (calcium ion) be added to a colloidal sol of arsenious sulphide or of gold,

<sup>1</sup> From the Greek *κατά* (*kata*), down, and *φέρειν* (*pherein*), to carry.

precipitation of the colloid takes place. A similar behaviour is found in the case of ordinary fine suspensions, *e.g.* of clay in water, and this is sometimes of considerable geological or geographical importance. Thus, the sedimentation of finely divided, water-borne clay is markedly influenced by the purity of the water transporting it, and takes place more rapidly when salts are present than when they are absent. This, indeed, is one reason for the rapid deposition of river mud on mixing with seawater, and for the consequent silting up of river mouths and the formation of deltas such as have taken place at the mouth of the Nile and of the Mississippi.

The electrical charge on a colloid particle may be neutralised not only by the ion of an electrolyte but also by another colloid carrying an electric charge of opposite sign. When a positively charged colloid, such as ferric hydroxide, is added to a negatively charged colloid, such as arsenious sulphide, adsorption takes place with formation of larger particles; and when the proportions of the two colloids mutually adsorbed are such as are just sufficient to produce an uncharged particle, complete sedimentation takes place. The relative amounts of the two colloids required for complete mutual precipitation will depend on the mutual adsorbability of the colloids and are fairly accurately defined. The composition of the precipitate obtained will consequently be, at least approximately, constant. The production of these adsorption complexes, as they have been called, simulates, therefore, the formation of a chemical compound and has sometimes been mistaken for a process of chemical combination. Thus, Purple of Cassius, known and used as early as the seventeenth century for the colouring of glass and enamels, is not a compound but an adsorption complex of stannic hydroxide and colloidal gold.

The process of adsorption plays an important and perhaps predominant part in the dyeing of textiles. In the case of the so-called acid and basic dyes, for example, one is dealing with the salt of a coloured acid ion (the dye ion being therefore negatively charged), or with the salt of a coloured basic ion (the dye ion being therefore positively charged). The more strongly positive the charge on the fibre, the greater will be the adsorption of a negatively charged or acid dye; and the greater the negative charge on the fibre, the greater will be the adsorption of a positive or basic dye. Since addition of acid increases the positive charge on the fibre, through adsorption of hydrogen ion, adsorption (and therefore the dyeing effect) of a negative or acid dye will be increased in acid solution; and, on the other hand,

positive or basic dyes will act most effectively, or be adsorbed most largely from alkaline solution.

In the case of what are called substantive dyes, the dye itself is in colloidal solution, and addition of electrolyte increases the adsorption of dye by diminishing the stability of the colloid, just as electrolytes bring about the precipitation of arsenious sulphide.

While it is found that, in very many cases, silk and wool have the power of taking up and fixing the dye-stuff directly, it is frequently found that in the case of cotton the fixation of the dye has to be assisted by a *mordant*, which is either a colloid itself or can give rise to a colloid. The colloid so formed is deposited on and within the fibre to be dyed, and attracts and fixes oppositely charged colloidal dyes. According to the nature of the dye, so must be the nature of the mordant employed, salts of aluminium, chromium, etc., which give rise to the hydroxides of the metals being used when the dye has a negative charge or has acid properties (*e.g.* alizarin); while tannic acid and similar substances are employed for dyes with a positive charge or with basic properties. After the dye has been adsorbed, secondary changes may take place which increase the stability of the adsorption complexes, and render the dye less easily removed.

In the process of tanning, also, there is formation of adsorption complexes between the hide—a positively charged colloidal gel—and the negatively charged colloid, tannin. The formation of the adsorption complex is followed by chemical changes whereby the process of leather production is completed.

Owing to the presence of such colloids as ferric hydroxide and aluminium hydroxide, filtration through soil acts as a very efficient means of purifying sewage and other waste water from organic impurities. These impurities in sewage, for example, have been found to be, to a large extent, negatively charged colloids and are therefore precipitated and retained by the positively charged colloids, ferric hydroxide and aluminium hydroxide. By such filtration through the soil, therefore, even the highly impure water which drains from cultivated and manured land is rendered comparatively sweet and harmless. In the same way, the purification of drinking-water by filtration through beds of sand or through charcoal, depends on the removal of impurities by adsorption on the large filtering surface exposed, and on the retention of positively charged colloidal matter, bacteria, etc., by the negatively charged sand or charcoal particles.<sup>1</sup>

<sup>1</sup> The rendering of sea-water potable by percolation through clay is mentioned by Aristotle.

An important application of the behaviour just described is found in sewage farms, where the drainage of towns is pumped on to the land and the liquid allowed to drain through the porous soil. Here, the waste organic matter is retained and affords a rich nutriment for the growing crops, while the liquid effluent which drains away is such that it might be drunk with safety. By such means can, in suitable surroundings, a source of annoyance and loss be turned to profit.

**Emulsoid Colloids.**—In the case of the emulsoid or lyophile colloids, such as gelatin, albumin, etc., the stability of the colloid, although partly due to an electric charge on the particles, is mainly due to adsorbed water or, speaking generally, to adsorbed dispersion medium. Such solutions, therefore, are not so sensitive to added electrolytes. Although the addition of small amounts of an electrolyte may produce changes in the amount of water adsorbed by the colloid, actual precipitation does not take place until the concentration of added electrolyte is relatively large.

The influence of electrolytes in altering the distribution of water between a colloid and its aqueous dispersion medium is of much importance in many biological processes and also in agriculture. Thus, although the presence of colloids is essential to the production of a good soil, too large a proportion of water-adsorbing colloid diminishes the fertility of the soil. By the addition of calcium sulphate (gypsum) to such a soil, a partial flocculation and diminution of the water-retaining power of the colloids are brought about, and the quality of the soil is thereby improved. A complete destruction of the colloidal properties of the soil, however, would greatly diminish its power to retain the water and salts necessary for the growth of vegetation, and must therefore be avoided.

The comparatively great insensitiveness to electrolytes, shown by hydrophile colloids of the gelatin type, may be transferred to hydrophobe or suspensoid colloids of the type of colloidal gold or arsenious sulphide.

When gelatin, for example, is added to a colloidal gold solution, the gold is adsorbed by the gelatin and a much greater concentration of electrolyte is required in order to precipitate the gold than is necessary in the absence of the gelatin. The gelatin is said to protect the gold. This so-called *protective action*, which varies greatly in different hydrophile colloids, is of much importance in many directions.

The water of the Mississippi and of the Nile is always turbid and muddy, owing to the presence of a large amount of colloidal

organic matter which stabilises the fine suspension of clay and soil; and it is only when the rivers reach the salt water of the sea, with its high concentration of salts, that the finely dispersed mud is precipitated and forms deltas.

The water of the Ohio River, on the other hand, is at all times clear, owing to the absence of protective colloids and the presence of lime and other salts which act as precipitating agents.

By the use of protective colloids, sparingly soluble substances, produced by chemical reaction, can be kept in the colloidal state and so prevented from undergoing flocculation and sedimentation. Thus, when dilute solutions of silver nitrate and potassium bromide are mixed, there separates out a white curdy precipitate of silver bromide which is, by reason of its coarseness, quite unsuitable for photographic purposes; but if gelatin is first dissolved in the solutions of silver nitrate and potassium bromide, no curdy precipitate but only a colloidal suspension of very fine particles is obtained on mixing the solutions.

The protective action of hydrophile colloids is also clearly seen in the nature of the curd which is formed from milk, and in the readiness with which it is formed on addition of acid or of rennet. In cow's milk there is a relatively large amount of casein and a relatively small amount of the protective colloid, lact-albumin. Cow's milk, therefore, readily curdles. In human milk, there is a smaller proportion of casein and a larger proportion of lact-albumin, so that the casein is more effectively "protected," and curdling takes place less readily. Human milk is, therefore, more readily digested than cow's milk. In ass's milk, the proportion of protective colloid to casein is highest of all, and curdling, therefore, takes place still less readily, and the digestibility of ass's milk is greatest of all. By increasing the proportion of protective colloid in cow's milk by the addition, for example, of gelatin, white of egg, or even barley water (containing starch), the formation of a curd in the stomach may be more or less completely prevented; and the curd, if formed, is less compact. The digestibility of the milk is thereby increased.

In the manufacture of ice cream, likewise, protective colloids, like albumin (white of egg) and gelatin, are made use of owing to the fact that in their presence the casein is prevented from coagulating and the ice particles are kept very small. The ice cream, therefore, feels smooth.

Many colloidal sols, *e.g.* gelatin, agar, etc., when cooled or coagulated, pass into a jelly, owing to the coalescence of the hydrated colloid particles. The jelly so formed may be regarded as constituted by a honey-comb or network of hydrated colloid,

the meshes or cells of which are filled with a dilute solution of the colloid. The water-holding or liquid-holding power of such jellies is, sometimes, very great, as is seen from the fact that jellies have been obtained which contain less than 0.5 per cent. of the colloid. This property is made use of in the production of "solidified alcohol," a jelly formed by colloid calcium acetate in alcohol. The jelly is rendered more stable by addition of a small amount of stearic acid.

**Peptisation.**—Although the addition of an electrolyte, in certain concentrations, may bring about the precipitation or flocculation of a hydrophobe or suspensoid colloid, it is found that very low concentrations of electrolyte may render the colloid more stable. Similarly, it is found that small quantities of electrolyte may facilitate the dispersion of a substance and so produce a colloidal sol. This process of deflocculation, which is the reverse of flocculation or agglomeration of particles, is often spoken of as *peptisation*, on account of its superficial resemblance to the process of conversion of insoluble protein into soluble or colloiddally dispersed peptone. The peptising action of electrolytes is due to the preferential adsorption of one ion of the electrolyte, so that the colloid particle acquires a positive or negative charge. Thus, clay and silicic acid can be peptised or caused to pass into colloidal solution by shaking with a very dilute solution of alkali (containing hydroxide ions).

Peptisation may also be brought about not only by the adsorption of ions, but by adsorption of liquids or of hydrophile colloids. Thus, cold water peptises tannin and soap, hot water peptises gelatin. Cellulose nitrate (collodion cotton) is peptised by a mixture of alcohol and ether, thus giving collodion. Even when adsorbed substances may not, in themselves, be able to peptise solids, they may, by acting as stabilisers and as protective colloids, assist mechanical or other processes in the production of the colloidal state. Thus, as Dr. E. G. ACHESON found a number of years ago, when graphite is ground with a solution of tannin, a colloidal sol of graphite can be obtained, the so-called *deflocculated Acheson graphite* ("Dag"), which is largely employed as a lubricant.

The production of colloiddally dispersed or deflocculated materials by grinding in special colloid mills in presence of protective colloids or "dispersators," is now a considerable industry. Such very finely divided materials find application in the paint industry and as "fillers" in paper, rubber, etc.

## CHAPTER XXVI

### THE RISE OF ORGANIC CHEMISTRY

Down nearly to the end of the seventeenth century, chemists interested themselves almost entirely in the substances occurring in the non-living mineral world, but in his celebrated and widely read *Cours de Chymie*—the first clearly written text-book of chemistry—the French physician and chemist, NICOLAS LEMERY (1645–1715), brought the substances occurring in plants and animals also within the ambit of chemical interest and investigation. Towards the end of the eighteenth century one applied to such substances, on account of their association with living or “organised” matter, the term *organic*, thereby distinguishing them from the *inorganic* substances which make up or which can be formed from inanimate, mineral matter.

For long, chemists drew a sharp distinction between these two classes of compound—the inorganic and the organic. It had, it is true, been shown by Lavoisier that organic compounds are composed, for the most part, of the elements carbon, hydrogen, oxygen and nitrogen—elements which occur in purely inorganic or mineral compounds—but it was thought that the power of building up these elements into the complex compounds occurring in the animal and vegetable organism, was the sole prerogative of the so-called *vital force*, or vital energy, inherent in the living cell. Moreover, although Berzelius was able to show, in 1815, that the composition of organic compounds follows the laws of constant and definite proportions and can be represented by molecular formulæ as in the case of inorganic compounds, yet, even as late as 1827, he upheld the view that while inorganic compounds could be prepared artificially in the laboratory, organic compounds could be produced only in the living animal or vegetable organism. The foundations of this belief, however, were already being sapped, and in the following year the German chemist, FRIEDRICH WÖHLER (1800–1882), who in 1836 became Professor of Chemistry in the University of Gottingen, could write to Berzelius these momentous words—words which may be regarded as announcing the birth of modern organic chemistry :



"I must tell you that I can make urea without the need of kidneys or of any animal whatever."

It was in 1828, while a school teacher in Berlin, that Wöhler accomplished what was, perhaps, the most important work of his life, the conversion of ammonium cyanate into urea. On heating a solution of ammonium cyanate, a compound not produced in the living organism, there was formed, as Wöhler discovered, the substance urea. This compound occurs in urine and had hitherto been known only as the product of animal metabolism. By the discovery that a distinctively organic compound produced in the animal organism could be formed from non-living material without the aid of the living organism, the gulf which had seemed to separate the compounds of the mineral world from those of animate nature, was bridged.

This synthesis of an organic compound from inorganic material, which remained for a number of years the only one of its kind, received, about the middle of last century, abundant support and confirmation, so that the belief in the necessity of a vital force for the synthesis of organic substances could no longer be held. Although all the substances which occur in the animal and vegetable organism have not yet been prepared artificially, a sufficiently large number have been synthesised to dispel all doubt as to the theoretical possibility, at least, of artificially preparing all, and to show that chemical formations and transformations are governed by the same laws in animate as in inanimate nature.

From the work of Wöhler and of those who followed him, it became clear that no distinction between inorganic and organic compounds could be justified on the basis of origin or association with a living organism. Nevertheless, for the purposes of classification, it has been found justifiable and convenient to draw such a distinction on the basis of the chemical behaviour of the element carbon itself, an element which is present in all the compounds formerly classed as organic. The term "organic" is therefore retained, but with an altered connotation, for by "organic compound" one now means simply a compound of carbon, and by organic chemistry, the chemistry of the compounds of carbon. Under the heading of organic compounds, therefore, there are included not only the compounds formerly regarded as organic—compounds associated with the living animal or vegetable organism—but also all those much more numerous compounds of carbon which have been produced synthetically in the laboratory.

Such a classification, which, like all classifications in science,

has been made as a matter of convenience and for the purpose of facilitating the mastery and advancement of knowledge, is amply justified by the number of compounds which fall to be classed as organic; for the number of carbon compounds now amounts to something like a quarter of a million. Further justification for the separation of the compounds of carbon into a special class is found in the fact that in their case one meets with a phenomenon which, although encountered in the case of the compounds of other elements, is found with extraordinary frequency in the case of the compounds of carbon. This is the phenomenon to which the name *isomerism*<sup>1</sup> has been given.

**Isomerism and Constitution.**—When Dalton introduced his atomic theory, the basis on which all modern chemistry has been built, he showed, as we have seen, that a compound could be regarded as being formed by the combination or uniting of the atoms of the constituent elements in certain constant and definite proportions. While, however, the law, “One compound, one composition,” has remained unshaken, the progress, more especially of organic chemistry, soon showed that the converse statement, “One composition, one compound,” which, to the earlier chemists, was equally an article of faith with the former, is very far removed from the truth. This fact first forced itself on the attention of chemists when JUSTUS VON LIEBIG (1803–1873), showed by analysis that the highly explosive compound silver fulminate,  $\text{CNOAg}$ , which he had prepared, had a composition identical with that of the harmless, non-explosive silver cyanate which had been prepared by Wöhler. In other words, two compounds with markedly different properties were found to have the same composition, and to this new phenomenon there was given, on the suggestion of Berzelius, the name *isomerism*. As the number of carbon compounds became multiplied, the phenomenon of isomerism was more and more frequently observed, so that more than a hundred different compounds, for example, can be produced by the combining together of nine atoms of carbon, ten atoms of hydrogen and three atoms of oxygen ( $\text{C}_9\text{H}_{10}\text{O}_3$ ). The existence of isomeric compounds can be explained by a difference in the arrangement of the atoms in the molecule, for, just as the same set of bricks can, by varying their arrangement, be formed into structures of very different kinds, so also the same atoms can, by varying their arrangement within the molecule, give rise to different atomic structures or different compounds.

The discovery of isomerism, so entirely unforeseen by Dalton,

<sup>1</sup> From the Greek *ἴσος* (isos), equal, and *μέρος* (meros), a part.

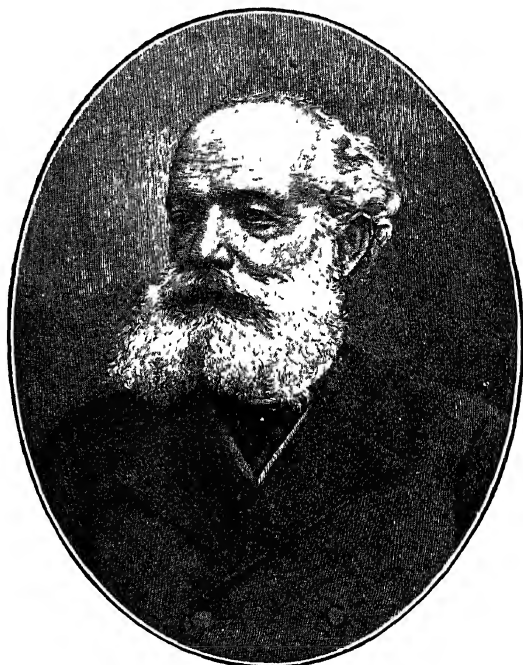
led to the recognition of the fact that the properties of a compound depend not merely on its composition, or the nature and number of the elements combined together, but also on its internal structure or the arrangement of the atoms within the molecule. Our knowledge of an organic compound, therefore, cannot be complete unless we know, not only its composition but also its internal structure or *constitution*; and the determination of the structure or constitution of compounds is one of the most important problems with which the investigator in organic chemistry is confronted.

A knowledge of the constitution is essential, also, for the successful carrying out of those processes of synthetic chemistry, or the building up of more complex from simpler molecules, to which we owe the existence of the vast array of dyes, drugs, medicinal chemicals, etc., derived from the simpler compounds obtained from coal tar and from other raw materials. The problem of elucidating the constitution or of unravelling the architecture of organic compounds may be, in the case of the more complex compounds especially, one of the greatest difficulty, and it requires for its solution great mental acumen, a profound knowledge of chemical behaviour and a highly developed scientific imagination. With regard to the general method of attack, only this much can be said here. Through the laborious efforts of numberless chemists, a knowledge has been gradually accumulated of the internal structure or constitution of a very large number of substances, and also of the relations between these different structures and the physical and chemical properties of the compounds. In order to determine the constitution of an unknown compound, therefore, the molecule of the substance is, by various chemical reactions, broken into bits, as it were, and one then seeks to identify the fragments, the simpler substances, so obtained, with substances of which the constitution is already known. From the knowledge gained in this way, one may then attempt to piece the fragments together again, and so build up or synthesise the original substance.

**Theory of Molecular Structure.**—The task of interpreting the results of experiments, of understanding the relations between the multitude of organic compounds and of elucidating their constitution would, however, be a hopeless one without the aid of some guiding principle and some method by which the molecular constitution can be represented. Throughout the first half of the nineteenth century, various theories of molecular structure were put forward by some of the most eminent chemists of the day, but it was not until after Frankland had, in 1852,

put forward his theory of valency (p. 66), that a satisfactory theory of molecular structure could be advanced. Such a theory was put forward independently, in 1858, by two young chemists, FRIEDRICH AUGUST KEKULÉ and ARCHIBALD SCOTT COUPER.

FRIEDRICH AUGUST KEKULÉ was born at Darmstadt in 1829 and displayed, even as a boy, unusual ability especially in mathematics and drawing. After passing through the *Gymnasium* of his native town, he entered the University of Giessen as a student of architecture, and his architectural studies gave



FRIEDRICH AUGUST KEKULÉ.

a permanent bent to his mind. At that time, Liebig was Professor of Chemistry at Giessen, and Kekulé attended his lectures; and so strongly was he attracted by the subject that he abandoned the architecture of masonry for the architecture of molecules, for it was on the development of the theories of molecular structure that he was destined to leave the chief impress of his genius. Kekulé studied for a year in Paris under Dumas, and for some years thereafter held private research posts in Switzerland and in London. In 1856, Kekulé became a Privatdozent at Heidelberg; in 1858, Professor of Chemistry at Ghent; and in 1867,

Professor of Chemistry at Bonn. Accepting the dictum of his master, Liebig, that "no one who does not ruin his health with study will ever do anything in chemistry nowadays," Kekulé, during many years, allowed himself no more than three or four hours sleep nightly. And Nature took her revenge in a premature decay of his physical powers. One of the most celebrated of the German chemists of the nineteenth century, Kekulé received many conspicuous honours from Universities and learned Societies. He was ennobled by the German Emperor, and adopted the name of Kekule von Stradonitz (dropping the accent on the final *e* of his name). He died in 1896.

ARCHIBALD SCOTT COUPER was born at Kirkintilloch, near Glasgow, in 1831. After studying classics and philosophy at the Universities of Glasgow and Edinburgh, he studied chemistry first at Berlin and then at Paris. In 1858, he became an assistant in the Chemistry Department of the University of Edinburgh, but his scientific career was early terminated by a breakdown of health. He died in 1892.

Couper's theory of molecular structure, essentially the same as that of Kekulé, was published in France and remained for long unnoticed. The theory, therefore, became associated with the name of Kekulé only, but one must not now deny to the young Scottish chemist his share in the honour attaching thereto.

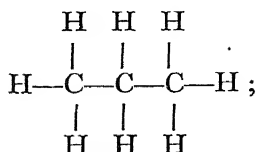
As the two main postulates of their theory of structure, Kekulé and Couper adopted the quadrivalency of carbon and the capacity of carbon atoms for mutual linking; and on the foundation of these two postulates they were able to show how the molecular constitution or the mutual linking together of the atoms of an organic compound, could be represented diagrammatically and the relations between different compounds made readily intelligible.

Although there is, of course, no material link or bond between the atoms, one can nevertheless represent union between atoms as if it were material, by means of a line, or lines, according to the valency of the atom. Thus, as we have already seen, the compound, marsh-gas, can be represented by the diagrammatic

H  
|  
H—C—H  
|  
H

or *graphic formula* H—C—H, and the higher hydrocarbons of

that series by such a chain of carbon and hydrogen atoms as



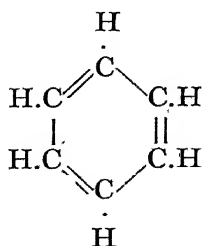
a formula which can also be written in the simpler, more condensed form,  $\text{CH}_3\text{—CH}_2\text{—CH}_3$ , called a *structural* or *constitutional formula*. By the extension of this idea, it became possible not only to represent the molecular constitution of known compounds, but also to foresee the possible existence of isomeric compounds. Thus, for example, in the case of the compound  $\text{CH}_3\text{.CH}_2\text{.CH}_3$  (the bond between the carbon atoms being now represented by a dot), it is clear that one can replace an atom of hydrogen in this compound by an atom, say, of chlorine, in two ways, so as to form either the compound  $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{Cl}$ , or the compound  $\text{CH}_3\text{.CHCl.CH}_3$ , the chlorine being, in the former case, attached to a terminal carbon atom, and in the latter case, to the intermediate carbon atom. Accordingly, there should exist two and only two different compounds having the composition  $\text{C}_3\text{H}_7\text{Cl}$ ; and as a matter of fact two compounds and only two are known.

In the same way, the isomerism between silver fulminate and silver cyanate, the first case of isomerism to be discovered, can be represented by the formulæ  $\text{Ag.O.N:C}$  (silver fulminate) and  $\text{Ag.O.C:N}$  (silver cyanate); and the relation between ammonium cyanate and urea is represented by the formulæ  $\text{NH}_4\text{.O.C:N}$  (ammonium cyanate) and  $\begin{array}{c} \text{H}_2\text{N} \\ \text{H}_2\text{N} \end{array} \text{>C:O}$  (urea). The origin of this theory of chemical structure has been recounted by Kekulé himself. During a period of residence in London he was returning from a visit paid at Islington to where he stayed at Clapham. "One fine summer evening," he relates,<sup>1</sup> "I was returning by the last omnibus 'outside' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time, I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two

<sup>1</sup> F. R. Japp, "Kekulé Memorial Lecture" (*Transactions of the Chemical Society*, 1898).

smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain. . . .” And then he adds: “I spent part of the night putting on paper at least sketches of these dream-forms.” From these sketches were developed the constitutional or structural formulæ, of which examples have just been given.

Although the molecules of a very large group of compounds, the *aliphatic*<sup>1</sup> compounds—so called because the natural fats belong to this class—can be represented as built up of chains of carbon atoms, many other compounds, belonging to the so-called *aromatic* or benzene series, cannot be so formulated; and one has to assume that in the case of these, the carbon atoms are joined together in the form of a ring. This conception of a ring structure for the benzene molecule is also due to Kekulé, and was put forward by him in 1865, also as the result of a “dream.” He was then Professor of Chemistry at Ghent, and was engaged one evening in writing his text-book, but his thoughts were elsewhere. “I turned my chair to the fire and dozed,” he relates. “Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation; long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke”; but the picture Kekulé had seen of the snake which had seized its own tail gave him the clue to one of the most puzzling molecular structures, the structure of the benzene molecule, a ring of six carbon atoms to each of which a hydrogen atom is attached. Thus we obtain the structural formula of the benzene molecule,



the “ring” of carbon atoms being written in the form of a

<sup>1</sup> From the Greek *ἀλειφαρ* (*aleiphar*), fat.

hexagon instead of in the form of a circle. "Let us learn to dream," said Kekulé, "then perhaps we shall find the truth." And he wisely added: "But let us beware of publishing our dreams before they have been put to the proof by the waking understanding." The confirmation by X-ray analysis of the hexagonal arrangement of carbon atoms in benzene is an impressive testimony to the wonderful insight of Kekulé and of his power of interpreting the behaviour of organic compounds.

Although, as will be pointed out later, the simple theory of Kekulé has been found to be inadequate, the conception of molecular structure and the method of structural representation introduced by Kekulé form the basis on which organic chemistry has developed; and they have not only enabled chemists to correlate the behaviour of a vast number of compounds but have also guided them to the discovery and preparation of new substances. For the advance and development of organic chemistry these theories of molecular structure have been of no less importance than are compass and chart to a mariner; and without them organic chemistry would have remained such as it was described by Wöhler, a "tropical forest primeval, full of the strangest growths, an endless and pathless thicket, in which a man may well dread to wander."

**Homologous Series.**—The mastery of organic chemistry would be an almost impossible task if it were not for the fact that the quarter of a million compounds of carbon already known can be grouped into a relatively small number of "homologous <sup>1</sup> series," the members of which are similarly constituted and have similar chemical properties. The molecular composition of successive members of a homologous series, we have already learned (p. 203), differs by  $\text{CH}_2$ , and, on the basis of the theory of Kekulé, the structural formula of each member can be derived by replacing one hydrogen atom in the formula of the preceding compound by the group  $\text{CH}_3$ . Thus, in the homologous series of *saturated hydrocarbons* (p. 202), by replacing one of the hydrogen atoms of ethane ( $\text{CH}_3\text{CH}_3$ ) by the group  $\text{CH}_3$ , one obtains  $\text{CH}_3\text{CH}_2\text{CH}_3$ , which is the formula of the hydrocarbon *propane*. If one now replaces one of the hydrogen atoms of propane by  $\text{CH}_3$ , it will be clear that one can obtain either  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  or  $\text{CH}_3\text{CH}(\text{CH}_3)_2$ , according as the hydrogen atom which is replaced



was attached to one of the terminal carbon atoms or to the middle carbon atom. Two isomeric *butanes* ( $\text{C}_4\text{H}_{10}$ ), therefore, can exist;

From the Greek  $\delta\mu\acute{o}\varsigma$  (homos), the same, and  $\lambda\acute{o}\gamma\omicron\varsigma$  (logos), proportion.



and it will be obvious that as one proceeds in a similar manner to the higher members of the series, the possible number of *isomers* or *isomerides* rapidly increases.

Besides the homologous series of saturated hydrocarbons, one may recall the corresponding series of *unsaturated hydrocarbons* of which the first member is ethylene,  $\text{CH}_2=\text{CH}_2$ , and acetylene,  $\text{CH}\equiv\text{CH}$ , respectively.

Since it is the purpose of this discussion merely to indicate and briefly to illustrate the more important general principles underlying the development of modern organic chemistry, it will be possible, in the following chapters, to allude to only a few of the more important homologous series of compounds, and to describe somewhat more fully one or two of the more important members of these series.

## CHAPTER XXVII

### THE ALIPHATIC COMPOUNDS

THE aliphatic compounds constitute one of the large groups into which the carbon compounds are classified, and their molecules may be regarded as built up of "chains" of carbon atoms, to which hydrogen or other atoms or groups of atoms are attached. The various homologous series of compounds belonging to this group, may be regarded as derived from the saturated hydrocarbons of the methane series (p. 420), or from the unsaturated hydrocarbons of the ethylene or acetylene series. For purposes of illustration, we shall consider only the saturated compounds.

#### I. HALOGEN DERIVATIVES

When the saturated hydrocarbons of the methane series are acted on by chlorine in presence of sunlight, one or more atoms of hydrogen are replaced or *substituted* by chlorine. Thus, from methane,  $\text{CH}_4$ , there is first formed the compound  $\text{CH}_3\text{Cl}$ , known as *methyl chloride*.<sup>1</sup> From ethane, similarly, there is formed *ethyl chloride*,  $\text{C}_2\text{H}_5\text{Cl}$ . From the homologous series of hydrocarbons, therefore, another homologous series of chlorides can be obtained.

On more prolonged action of chlorine, other atoms of hydrogen can be replaced, and so one obtains  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ .

The compound  $\text{CHCl}_3$  is well-known under the name of **chloroform**. It was first prepared by LIEBIG in 1831, and its narcotic action was discovered in 1847 by the Edinburgh physician, Sir JAMES YOUNG SIMPSON (1811–1870). Its general application as an anæsthetic in surgery followed soon after. This compound, which is a colourless, volatile liquid with a characteristic odour, is now generally prepared by the action of bleaching powder on alcohol (spirits of wine) or on acetone.

<sup>1</sup> The group of atoms,  $\text{CH}_3$ , left on removal of one atom of hydrogen from methane, is known as methyl, because it is present in the molecule of methyl alcohol (see later). Similarly,  $\text{C}_2\text{H}_5$  is known as ethyl. These, and similar groups of atoms, pass into and out of compounds as a single unit, just like an element, and are generally called *radicals*.

The analogous compound, **iodoform**,  $\text{CHI}_3$ , is an antiseptic and is used as a dressing in surgery.

## II. ALCOHOLS

When methyl chloride is acted on by silver hydroxide,  $\text{AgOH}$ , the chlorine atom is replaced by the hydroxyl-group ( $\text{OH}$ ), and the compound *methyl alcohol*,  $\text{CH}_3\text{OH}$ , is formed. This is the lowest member of another homologous series of compounds, known as *alcohols*, the term alcohol being generic and applied to organic compounds in which a hydroxyl-group, attached to a carbon atom, is present in the molecule.

The word "alcohol" which, when used without qualification, is applied to ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , or "spirits of wine," is derived from the Arabic *al-kohl*, the name given to the fine black powder of galena (lead sulphide) or of antimony sulphide, used from a very early period by Egyptian and other Eastern women to darken the eyebrows and eyelashes. At a later time, the word came to signify a very fine, subtle or impalpable powder, and hence, as PARACELSUS defined it, "the most subtle part of anything." It was with this significance, indeed, that Paracelsus introduced the term "alcohol vini" to denote the volatile "spirit" of wine obtained by distillation. Although applied at first to the alcohol obtained from wine, or ethyl alcohol as it is called, the term is now used generally for the whole class of compounds of which ethyl alcohol is the most important member.

**Methyl Alcohol,<sup>1</sup> Methanol or Wood Spirit.**—In his book, *The Sceptical Chymist*,<sup>2</sup> Boyle describes how, by the distillation of divers woods, he obtained a liquid which had "besides a strong taste, to be met with in the empyreumatical spirits of many other bodies, an acidity almost like that of vinegar," and how he found that from this "sourish liquor" there could be obtained another liquid which was, in an impure state, what is now known as methyl alcohol or "wood spirit," a substance which, until 1925, was produced commercially by the method employed by Boyle in 1661—that is, by the distillation of wood.

Since 1925, however, there has been developed, as has already been pointed out (p. 332), another process whereby methyl alcohol is now manufactured in large amount from a mixture of carbon monoxide and hydrogen (water gas), with the help

<sup>1</sup> The term methyl is derived from the Greek μέθυ (methy), wine, and ὕλη (hylē), wood. The name "methanol," which is in international use, indicates the relationship of methyl alcohol with methane, the termination, -ol, indicating an alcohol.

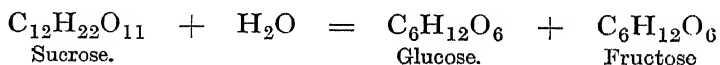
<sup>2</sup> Part III. (Everyman's Library Edition, p. 109.)

of a suitable catalyst. The wood distillation industry, an industry of great economic importance in various countries of the world, has thereby been dealt a serious and perhaps a mortal blow. This is, however, only one case out of very many where the economic life of a country has been more or less profoundly influenced by advances in chemical science.

Methyl alcohol is a colourless, volatile liquid which is more toxic than ordinary alcohol or spirits of wine. It is largely used in the manufacture of dyes, drugs, photographic chemicals, etc., and the crude wood spirit or *wood naphtha* is largely employed for "denaturing" ethyl alcohol.

**Ethyl Alcohol.**—Although various beverages containing ethyl alcohol were prepared at a very early time, it was not till the tenth or eleventh century that alcohol itself was obtained by the distillation of wine. At the present time, alcohol is produced commercially by the fermentation of various sugars, a process which, as has been pointed out (p. 328), is due to the catalytic activity of enzymes.

**Production of Ethyl Alcohol.**—Alcohol is produced by the action of a particular enzyme, *zymase*, on certain sugars, the most important of which is the sugar glucose which, along with the isomeric sugar, fructose, is found in sweet fruits and in honey. Zymase is secreted by the micro-organisms known as yeasts (*Saccharomycetes*), and when yeast is introduced into a solution of glucose, decomposition of the latter with production of alcohol and of carbon dioxide, is brought about through the agency of the zymase. Not all sugars, however, can be fermented by this enzyme. Thus, cane or beet-root sugar (known chemically as sucrose), and malt-sugar or maltose, are not fermentable with zymase. If, however, yeast is introduced into solutions of these sugars, fermentation does take place, owing to the fact that yeast secretes not only the enzyme zymase, but also the enzymes *invertase* and *maltase*. The former of these converts sucrose into the two simpler isomeric sugars, glucose and fructose, by a process of *hydrolysis* or decomposition through the interaction of water :



and maltase, similarly, converts maltose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , into glucose. The production of alcohol from sugars by means of yeast is, therefore, to be referred, in the last instance, to a fermentation of glucose (sometimes also of fructose) by zymase.

Fermentable sugars can be obtained not only from sucrose

(which is largely employed in France and in America in the form of beet-root molasses or cane-sugar molasses from Cuba), but also from starch, which constitutes, as a matter of fact, by far the most important raw material for the manufacture of alcohol. The starch is of varied origin. In Great Britain, it is derived mainly from maize, rice, wheat and barley, and in the United States, also, maize is largely used. In the future, cellulose, from wood-waste, may perhaps play a rôle of importance (p. 439). In Germany, most of the starch is derived from potatoes.

For the conversion of the starch into fermentable sugar, use is chiefly made of the enzyme *diastase*, contained in malt;<sup>1</sup> or, the starch is converted into glucose by heating with dilute sulphuric acid.

In the former case, the malt, which contains a considerable amount of starch and a small amount of sugar, together with the enzyme diastase, is crushed and mixed with hot water, and a quantity of raw grain or potato starch is added. By the action of the diastase, the starch is converted into maltose or malt-sugar. When this process of "mashing" is complete, the liquid is boiled to destroy the diastase, and the sweet liquor or "wort" is run into the fermenting vats and yeast is added. By the action of the enzyme maltase, which is contained in the yeast, the maltose is converted into glucose; and this, in turn, is converted by the yeast-enzyme zymase, mainly into alcohol and carbon dioxide, although small quantities of other substances—higher alcohols, succinic acid, etc.—are also produced.

Alcohol may also be produced by the action of yeast on commercial glucose, obtained by heating starch (e.g. potato starch) with dilute sulphuric acid, or on cane-sugar and beet-root sugar molasses (sucrose). In the latter case, conversion of the sucrose to the fermentable sugars, glucose and fructose, is effected by the yeast-enzyme, invertase.

The fermentation of the sugar solutions does not proceed indefinitely, and when the liquid contains from 10 to 15 per cent. of ethyl alcohol, the fermentation stops. The liquid, or "wash," as it is now called, contains not only ethyl alcohol, but also furfural and fusel oil—a mixture of higher-boiling alcohols, such as butyl alcohol,  $C_4H_9.OH$ , and amyl alcohol,  $C_5H_{11}.OH$ . From these different substances the ethyl alcohol is separated by distillation in special stills, by means of which a mixture of alcohol

<sup>1</sup> Many moulds, e.g. *Rhizopus Delemar* and *Mucor Boulard*, produce the enzyme diastase and are largely used in France and also to some extent in America, Spain and Italy, for converting starch into fermentable sugar. In this process, spores of the mould and yeast are added to the starch solution, and the processes of saccharification and of fermentation to alcohol go on side by side.

and water, containing about 96 or 98 per cent. of alcohol by volume, is directly obtained. Alcohol so obtained is spoken of as "silent spirit," or "patent still spirit." By allowing this alcohol to stand over quicklime for some time and then distilling, "absolute alcohol," or pure ethyl alcohol, is obtained.

For industrial and other purposes, alcohol finds abundant and varied use. Not only is it employed as a heating agent, in spirit lamps, but it is also used, to some extent, as an illuminant (with incandescent mantles), and as a motor fuel. Its relatively high cost, however, militates against any immediate and extensive development in this direction. Alcohol is also used very extensively as a solvent in the preparation of varnishes, lacquers and enamels; in the manufacture of ether, chloroform, acetic acid, celluloid, collodion, dyes, cordite and similar explosives, and many other substances. Ordinary *methylated spirit*, so largely used as a solvent and for other purposes, consists of ethyl alcohol "denatured" by the addition of wood-naphtha and mineral naphtha,<sup>1</sup> the presence of which is intended to render the liquid undrinkable.

From the fusel oils which are formed as by-products in the manufacture of ethyl alcohol, one can obtain propyl alcohol ( $C_3H_7.OH$ ), butyl and *iso*-butyl alcohol ( $C_4H_9.OH$ ), and amyl and *iso*-amyl alcohol ( $C_5H_{11}.OH$ ). These alcohols find their use not only in the scientific laboratory, but also in industry, for the purpose of preparing artificial fruit-essences, and as solvents.

**Alcoholic Beverages.**—Although ethyl alcohol is the most important constituent of alcoholic beverages, the taste, aroma and special character of each depend on the presence of small quantities of other substances, which differ both in amount and in kind according to the materials from which the beverage is prepared, and the method of its preparation. These beverages may be classed into distilled liquors (spirits), wines and beers.

In the case of *whisky*, the process of fermentation is carried out essentially as already described; malted barley, mainly, is employed, and the wash is distilled from a simple pot-still.

For the production of *gin*, the distilled spirit is flavoured by redistilling with juniper berries, coriander, fennel or other substances. *Brandy* is obtained by distilling wine, and owes its particular flavour to the various esters (see later) contained in the wine from which it is prepared; and *rum*, prepared from fermented molasses, owes its flavour chiefly to the esters, ethyl

<sup>1</sup> In the United States, methyl alcohol and benzene are used, and in Germany, methyl alcohol and pyridine bases, derived from coal tar.

acetate and ethyl butyrate. Sometimes it is also flavoured by placing the leaves of the sugar-cane in the still.

These distilled liquors all contain a high percentage, 40 to 50 per cent., or more, of alcohol.

*Wines* are prepared by the fermentation of fruit juices—chiefly the juice of the grape—in which the two sugars, glucose and fructose, are present. The juice also contains various acids, especially tartaric acid; and the skins of the grapes contain tannin, various essential oils, and, it may be, colouring matter. These all pass into the juice when the grapes are pressed, and according to their nature and relative amounts, give wines of different flavours and qualities.

The juice extracted from the grape is called “must,” and through its fermentation by a species of *saccharomyces* which grows on the grape itself, alcohol is produced. After the first “active fermentation” is over, the “new wine” is drawn into casks which are filled full and loosely closed. In the casks, a “still fermentation” proceeds for several months, during which time the yeast settles down, and the tartaric acid, along with various salts and colouring matters, separates out as *argol*. This consists chiefly of potassium bitartrate or potassium hydrogen tartrate,  $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$ , and is the main source of this salt, which is known familiarly as *cream of tartar*.

After the wine has become clear, it is drawn off into casks, and allowed to ripen for perhaps two or three years. During this process, the tannin and some other impurities are precipitated, and at the same time the alcohol and fusel oil combine with the small quantities of acids present to form esters, which give the peculiar and characteristic flavour and “bouquet” to the wine.

For the production of *beers*, malted grain is employed, but in the mashing process the complete conversion of the starch into maltose is not allowed to take place, a portion being converted only into the intermediate product of hydrolysis, *dextrin*.<sup>1</sup> This dextrin is retained in order to give “body” to the beer. Further, the nitrogenous compounds, the albuminoids and proteins, in the grain, are converted by the malt-enzyme, *peptase*, into peptones and other substances, which also add “body” to and increase the nutritive properties of the beer. All these various substances are classed together under the name “extract.” When mashing is complete, the wort is drawn off and boiled

<sup>1</sup> Dextrin is also produced industrially by heating starch with dilute sulphuric acid. It is used as an adhesive on stamps, envelopes, etc. It constitutes the so-called “British gum.”

with hops, and, after settling, the clear liquid is fermented with yeast.

### III. ALDEHYDES AND KETONES

When one writes the formulæ of methyl alcohol and ethyl alcohol in the form  $\text{H} \cdot \text{CH}_2 \cdot \text{OH}$  and  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$ , it is seen that in each case there is present the group  $-\text{CH}_2 \cdot \text{OH}$ . On subjecting such alcohols to the action of not too powerful oxidising agents, two atoms of hydrogen are removed, the group  $-\text{CH}_2 \cdot \text{OH}$  being oxidised to  $-\text{CHO}$  or  $-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{H} \end{smallmatrix}$ . The compounds so obtained are known as *aldehydes*,<sup>1</sup> and the group  $-\text{CHO}$  is known as the aldehydic group. From the homologous series of alcohols, therefore, one can form a homologous series of aldehydes. Owing to the readiness with which they undergo oxidation, the aldehydes act as reducing agents.

When one considers the alcohols higher in the series than ethyl alcohol, one finds that besides the alcohol with the group  $\cdot \text{CH}_2 \cdot \text{OH}$ , there is also an isomeric alcohol with the group  $:\text{CH} \cdot \text{OH}$ . Thus, there are two isomeric propyl alcohols, represented by the formulæ  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  (so-called normal propyl alcohol), and  $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{CH} \cdot \text{OH}$  (so-called *iso*-propyl alcohol). If now, one oxidises *iso*-propyl alcohol, the group,  $:\text{CH} \cdot \text{OH}$ , is converted, by the removal of two hydrogen atoms, to the group  $:\text{CO}$ , and the compound so formed is known as a *ketone*. A similar behaviour is shown by all other alcohols in the molecule of which the atoms are linked so as to form the group  $:\text{CH} \cdot \text{OH}$ .

**Formaldehyde**,  $\text{H} \cdot \text{CHO}$ , is the lowest member of the series of aldehydes, and is obtained from methyl alcohol by oxidation with atmospheric oxygen, the oxidation being catalytically accelerated by means of copper.

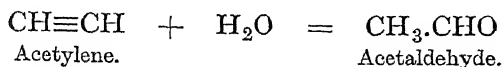
Formaldehyde is a gas under ordinary conditions, and so is placed on the market in the form of an aqueous solution known as *formalin*. It is used for disinfecting purposes, for preserving anatomical specimens, for the manufacture of dyes and of a plastic material known as *bakelite*. It converts the casein of milk into a hard bone or horn-like material, called by various trade names, such as *galalith*, *erinoid*, etc. This material, although hard and tough when cold, can be readily moulded when warm, and is used in the manufacture of a great variety of small articles—buttons, beads, combs, electrical fittings, etc.

**Acetaldehyde** can be obtained by the oxidation of ethyl

<sup>1</sup> Formed by contraction from al(cohol) dehyd(rogenatus).



alcohol, and is also produced commercially by the hydration of acetylene. In this process, acetylene is passed into a warm dilute solution of sulphuric acid in presence of mercuric sulphate, which acts catalytically. The acetylene combines with water to form acetaldehyde :



**Acetone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ , may be taken as a representative of the ketones. It is present in the aqueous distillate from wood (*pyroligneous acid*), from which mainly it is obtained. It may also be produced by the fermentation of starch (from maize, horse chestnuts, rice, etc.), by means of a special bacterial culture discovered by AUGUSTE FERNBACH, of the Pasteur Institute, Paris.

It is a colourless volatile liquid, which is very widely used as a solvent in the preparation of cordite, collodion, varnishes, etc. The ketones differ from the aldehydes in not being reducing agents.

#### IV. ACIDS

By the action of oxidising agents on aldehydes, the group  $-\text{CHO}$  is converted into the group  $-\text{COOH}$ , known as the *carboxyl* group; and the compounds so formed are found to yield solutions which have an acid reaction. The hydrogen atom of the carboxyl group can be replaced by a metal, with formation of a salt. Thus, when formaldehyde,  $\text{H}\cdot\text{CHO}$ , is oxidised, one obtains **formic acid**,  $\text{H}\cdot\text{COOH}$ , a substance known since the seventeenth century as being secreted by ants.<sup>1</sup> It is also contained in the stinging hairs of the common nettle. It is a colourless, corrosive liquid, which produces blisters when brought in contact with the skin.

Formic acid is the lowest member of a homologous series of acids which are known as the *fatty acids*, because of the fact that some of the higher members of the series, *e.g.* palmitic acid,  $\text{C}_{15}\text{H}_{31}\cdot\text{COOH}$ , and stearic acid,  $\text{C}_{17}\text{H}_{35}\cdot\text{COOH}$ , are found combined in the important naturally occurring compounds, the *fats*.

Apart from these higher acids, the most important member of the series is acetic acid.<sup>2</sup>

**Acetic Acid**,  $\text{CH}_3\cdot\text{COOH}$ , was the only acid known to the ancients, and to them it was known only in the form of a dilute solution. It was not till 1723 that the nearly pure acid was

<sup>1</sup> The name, formic acid, is derived from the Latin *formica*, an ant.

<sup>2</sup> From the Latin *acetum*, vinegar.

obtained by STAHL, and not till 1802 that the identity of the acid from vinegar with that from pyroligneous acid was established.

It is from pyroligneous acid, the aqueous product of the distillation of wood, that acetic acid is mainly obtained, the calcium acetate which is formed by the addition of milk of lime to pyroligneous acid being distilled with sulphuric acid. Acetic acid distils over and, when purified, forms a colourless, pungent-smelling liquid which crystallises at  $17^{\circ}$  C. in ice-like crystals. For this reason, the pure acid is spoken of as *glacial* acetic acid.

More recently, another process for the commercial production of acetic acid has begun to come into prominence. It has been pointed out that when acetylene is passed into a dilute solution of sulphuric acid in presence of mercuric sulphate, acetaldehyde is formed; and if air or oxygen is passed into liquid acetaldehyde in the presence of solid manganese acetate, oxidation of the aldehyde to acetic acid readily takes place.

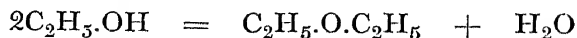
Many weak alcoholic beverages, such as light wines, become sour when exposed for some time to the air. This souring is due to the conversion (by oxidation) of the alcohol to acetic acid by the oxygen of the air, a change which takes place with special readiness under the influence of certain moulds and bacteria (*e.g.* *Mycoderma aceti* and *Bacterium aceti*). The process is carried out on a large scale for the production of *vinegar*.

## V. ETHERS AND ESTERS

The alcohols, which contain the hydroxyl group (OH), behave, in certain cases, *analogously* to the metal hydroxides. Thus, if water is removed from a metal hydroxide, the oxide of the metal is obtained. Copper hydroxide, for example, on being heated, loses water and passes into copper oxide:



So also one finds that when the elements of water are removed from an alcohol, an oxide is produced—the oxide so obtained being known as an *ether*. In this case, the elements of water can be removed by sulphuric acid, and so when ethyl alcohol is heated with concentrated sulphuric acid and then further amounts of alcohol slowly added to the mixture (Fig. 80), diethyl ether<sup>1</sup> distils over continuously:



**Diethyl Ether**, or ordinary ether, is a colourless, very volatile

<sup>1</sup> The radical  $\text{C}_2\text{H}_5$  was called *ethyl* because it occurs in ordinary ether.

liquid, the vapour of which is readily inflammable. It is used as a local anæsthetic, because, when sprayed on the skin, it evaporates rapidly and produces an intense local cooling; and it is also used as a general anæsthetic because complete anæsthesia is produced by inhalation of its vapour. Ether finds widespread use, also, as a solvent.

When methylated spirit is used in the preparation of ether, *methylated ether*, in which diethyl ether is mixed with small quantities of methyl ether, is obtained.

In another direction, also, the behaviour of alcohols is analogous to that of metal hydroxides. Thus, when potassium hydroxide is added to an acid, neutralisation takes place and a

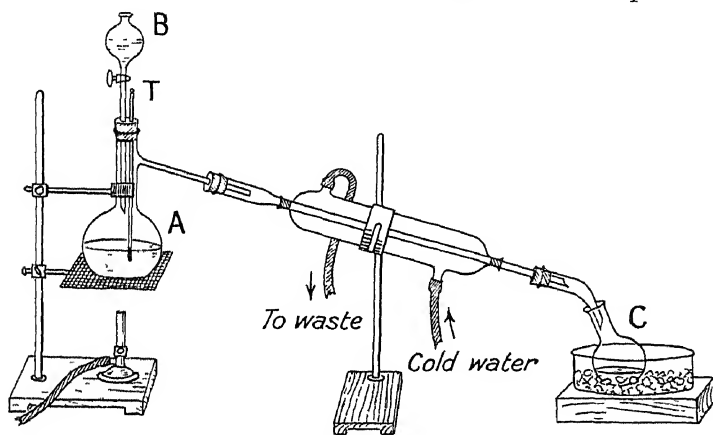
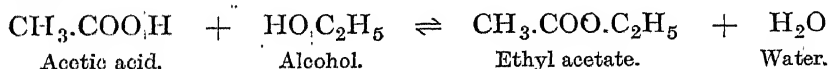


FIG. 80.—Preparation of ether.

The mixture of alcohol and sulphuric acid is heated in the flask A, and alcohol is run in from the funnel B. Ether distils over and is collected in the flask C, which is cooled in iced water. T is a thermometer.

salt and water are formed. So, also, when an alcohol reacts with an acid, whether an inorganic or an organic acid, water is eliminated and a compound, known as an *ester*, is produced. Thus:



(The dotted frame in the equation indicates the points from which the elements of water are removed. The residues,  $\text{CH}_3\text{COO}\cdot$  and  $\text{C}_2\text{H}_5\cdot$ , then unite to form the ester.)

The reaction between an alcohol and an acid, unlike that between an alkali and an acid, takes place only slowly and incompletely, and the product of the reaction, the ester, is a non-electrolyte.

The process of *esterification*, as it is called, is a very typical case of a reversible or balanced reaction (p. 320), leading to an equilibrium. In order to make the reaction as complete as possible, the water which is formed must be removed; the alcohol and acid are therefore heated together in presence of a small quantity, say, of concentrated sulphuric acid.

If, in the above reaction, the concentration of the water be increased, the reaction will, in accordance with the law of mass action (p. 318), be caused to take place from right to left; that is, ester and water will react to regenerate acid and alcohol. This is a process of *hydrolysis*, and is catalytically accelerated by acids and, in still greater measure, by alkalis. When the hydrolysis of an ester is carried out in presence of alkalis, the acid combines with the alkali, and a salt is formed. Since, as we shall see presently, this is essentially the process which takes place in the production of soap, hydrolysis of an ester in presence of an alkali, is spoken of as *saponification*.<sup>1</sup>

The esters are a very important class of compounds in organic chemistry. Many of them occur naturally in the sweet-smelling ethereal oils of plants, such as oil of wintergreen (the methyl ester of salicylic acid); and a number of the simpler esters of the fatty acids are manufactured, on account of their characteristic odours or flavours, for use as artificial fruit essences and flavourings. Thus, ethyl butyrate ( $C_3H_7.COO.C_2H_5$ ) is an artificial essence of pine-apple, amyl acetate ( $CH_3.COO.C_5H_{11}$ ) forms the main constituent of artificial essence of pears. It is to the presence of esters, as we have seen, that the characteristic flavour and "bouquet" of wines are due.

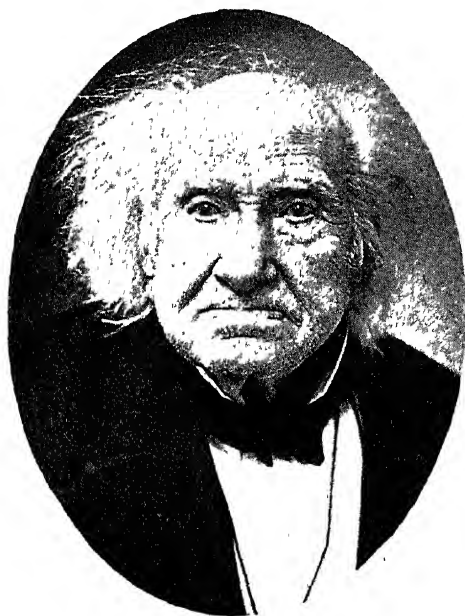
The natural animal and vegetable fats and oils, which are among the most important naturally occurring organic substances, are also esters, derived, however, not from an alcohol of the methyl alcohol series, but from glycerol (or glycerine),  $C_3H_5(OH)_3$ .

**Natural Fats and Oils.**—Although animal and vegetable fats and oils have been known from earliest times, it was not till early in the nineteenth century that the chemical nature and composition of these substances were elucidated by the French chemist, MICHEL EUGÈNE CHEVREUL, who was born at Angers in 1786. After acting for some years as assistant at the Natural History Museum in the *Jardin des Plantes*, at Paris, he was appointed, in 1813, teacher of chemistry at the Lycée Charlemagne, and later became Director of the Gobelins tapestry works. Here he carried out researches in colour contrasts. In 1830,

<sup>1</sup> From the Latin *sapo*, soap, and *facere*, to make.

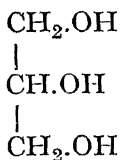
he became Professor of Organic Chemistry at the Natural History Museum, the Directorship of which he assumed in 1863. His scientific work covered a wide range, and his best-known work is his researches on animal fats. His hundredth birthday was celebrated with public rejoicings; and he was accorded a public funeral when, after a life which is unique in the annals of chemistry for its length and distinction, he died in Paris in 1889.

By his researches, carried out between 1811 and 1823, Chevreul showed that the fats and oils could, by appropriate

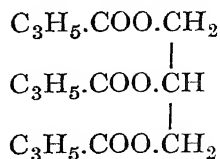


MICHEL EUGÈNE CHEVREUL in his 100th year.

reagents, be hydrolysed to glycerine and various acids. In other words, fats and oils are glyceryl esters of various acids. The alcohol, glycerol, to give it its systematic name, contains not one hydroxyl group, like methyl or ethyl alcohol, but three hydroxyl groups, its composition and constitution being represented by the formula :



Consequently, glycerol can react with three molecules of an acid to form an ester. Thus, with butyric acid,  $C_3H_5.COOH$ , for example, one obtains the ester, glyceryl butyrate,



which forms the main constituent of butter fat. The solid animal fats are mainly glyceryl esters of the saturated palmitic and stearic acids,<sup>1</sup> but the vegetable oils are mainly glyceryl esters of unsaturated acids, such as oleic acid,  $C_{17}H_{33}.COOH$ , an acid which contains two atoms of hydrogen less than stearic acid.

Fats and oils are among the most valuable of foodstuffs on account of the large amount of heat energy which they yield when they undergo slow oxidation in the body. Fats, indeed, yield twice as much heat energy as an equal weight of sugar or protein, and being more slowly oxidised than sugar, fats are particularly valuable when prolonged or sustained effort has to be made.

**Soap.**—The use of natural fats and oils for the manufacture of soap is second only in importance to their use as a food. According to Pliny, soap is a Gallic invention, but it would appear rather to have been first made in Germany from goat's tallow and beechwood ashes, the potassium carbonate in the latter being first converted to caustic potash by means of slaked lime. The material thus obtained, resembling a modern soft soap, was largely used as an ointment; and it was only in the second century of our era that it began to be used for detergent purposes. Even as early as the year 1000 A.D., Marseilles, the centre of French soap manufacture, had a flourishing soap industry, and, in the fourteenth century, soapmaking was commenced in England. In spite of the industrial development of soapmaking, household production of soap from the fat and grease saved from cooking, was still carried on in country districts of America about the middle of last century; and the method employed was probably very similar to that used nearly two thousand years ago. It is thus described by one<sup>2</sup> who had witnessed the process: "An old cask with one head was selected. Numerous auger

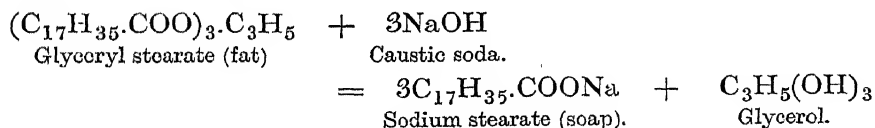
<sup>1</sup> Fats also contain mixed esters, or esters in which different acids are combined with glycerol.

<sup>2</sup> M. H. Ittner: *Chemistry in Industry*, Vol. 2, Chap. 21.

holes were bored in the head and the cask was then filled with alternate layers of straw and mixed lime and wood ashes. The cask was placed on a raised, slanting, grooved board. From time to time, a pail of water was poured upon the contents of the cask, and eventually a brownish liquid began to emerge and was collected in a pail and transferred to an iron pot. A chemical action took place which converted *potash*, the chief ingredient of the wood ashes, into *caustic potash*; and the brownish liquid or lye was then boiled in an open iron pot over a fire, out of doors, with the fat or grease until the experienced eye of the soapmaker looked upon it as finished. The fire was then allowed to go out and the contents of the pot left to chill to a solid mass, after which it was cut into bars of odd shapes which were none too firm." So, also, in all probability, did the father of Benjamin Franklin make soap at Boston towards the end of the seventeenth century.

A soap may be defined as a salt of the fatty acids. The sodium and potassium salts are soluble in water, and are used for detergent purposes; but the salts of calcium, magnesium, aluminium, etc., are insoluble. Aluminium soaps, which are used for rendering cloth waterproof, are formed by adding alum (potassium aluminium sulphate) to a soluble soap. Generally speaking, soda soaps are hard, and potash soaps soft.

For the production of a hard or soda soap, fat is boiled with caustic soda lye in a *soap pan* or *soap kettle*, the liquid being heated by means of steam. Thereby the fat, a glyceryl ester as we have seen, is hydrolysed or saponified, the process being represented by the equation:



When saponification of the fat is complete, a concentrated solution of common salt is added which causes the soap or sodium salt of the fat acid to separate out as a curd, while the glycerol, set free by the saponification, remains dissolved in the lye. The lye is run off from the soap curd and the latter boiled up with water to remove impurities, and again "salted out." It is then hardened by cooling, dried, cut into flakes, mixed with colouring matter or perfume, and formed into bars. The bars are then cut and moulded into tablets.

The familiar transparent soaps are obtained by dissolving pure soap in alcohol, and then evaporating off the alcohol.

In the manufacture of soft or potash soap, different animal or vegetable oils, *e.g.* linseed oil, cotton-seed oil, soya-bean oil, are saponified with caustic potash. A thick paste is thus obtained which, owing to the presence of glycerine derived from the oil, does not dry up.

The **glycerol** which is formed as a valuable by-product of soap manufacture is a thick, colourless, syrupy, hygroscopic liquid which mixes with water in all proportions, and has a sweet taste. Although it finds its main use in the manufacture of explosives, *e.g.* "nitroglycerine," which is the glyceryl ester of nitric acid, or  $C_3H_5(NO_3)_3$ , glycerol is also used as an emollient and for adding to the radiator-water of motor cars to prevent freezing.

**Soap as a Detergent.**—The cleansing power of soap depends on its physical as well as on its chemical properties; and in this connection its most important property is that it lowers the surface tension of water (p. 116). By thus lowering the surface tension, soap enables the water to wet and so to come into close contact with even a greasy surface. There is, however, another property of soap solutions which plays, perhaps, the most important part of all in the cleansing process. This is the property of emulsifying oils and fats. When an oil is vigorously shaken with water, it is found that a milky liquid is obtained owing to the oil being broken up into a large number of droplets. But this milky appearance is not permanent; in the course of a few minutes the droplets of oil run together to form larger drops, which then collect as a separate layer on the surface of the water. The milkiness thus disappears. If, however, the oil is shaken not with pure water but with water containing a little soap, the droplets into which the oil breaks up are much smaller (the emulsion appearing, in consequence, much whiter than before), and they do not run together and form a separate layer on standing. The oil is permanently emulsified. And this is what happens when soap is used in cleansing a greasy surface to which dust and other dirt so readily adhere; the film of grease is broken up owing to the emulsifying action of the soap solution, and the grease and dirt are then readily washed away. The removal of dirt is also facilitated in a purely mechanical way by the lather or foam which the soap-water forms, the production of lather being another result of the lowering of the surface tension of water.

**Hydrogenation of Oils.**—As a consequence of the great development of the margarine industry, the supply of solid animal fats available for the manufacture of soap was greatly



diminished, and it became, therefore, a matter of importance to discover a method by means of which liquid oils could be converted into solid fats. Theoretically, the process is a simple one. Oleic acid,  $C_{17}H_{33}.COOH$ , for example, differs from stearic acid,  $C_{17}H_{35}.COOH$ , only in the fact that it contains less hydrogen. It is what has been called an unsaturated compound. By adding the proper amount of hydrogen, therefore, to oleic acid, one could convert it into the solid stearic acid; or, on the other hand, by adding hydrogen to liquid glyceryl oleate, the oil could be converted into the solid fat, glyceryl stearate, and other oils could similarly be converted to fats. Although it was not difficult to carry out such a conversion in the laboratory, a commercially successful process could be developed only when, in 1899, it was found by the French chemists, PAUL SABATIER and JEAN BAPTISTE SENDERENS, of the University of Toulouse, that finely divided nickel acts as an efficient catalyst. In the presence of this metal, the liquid oils—olive oil, linseed oil, fish oil, etc.—combine with gaseous hydrogen and are converted into solid fats; and by this process of hydrogenation, large quantities of fats are now produced for use in soap manufacture and also for the preparation of edible fats.

Not only does the process of hydrogenation of oils, which has already developed into an important industry, secure a fresh source of raw material for the manufacture of an article of such importance in our modern civilisation as is soap, but by stimulating the cultivation of oil-producing plants it will exercise a profound influence on the economic development of those countries which are suitable for such cultivation.

## VI. CARBOHYDRATES

Reference has already been repeatedly made to sugars, starch and cellulose, and to the use of these substances in the fermentation and explosives industries. The compounds are important products of plant life, and when their composition is determined, it is found that they all belong to a group of compounds consisting of carbon, hydrogen and oxygen, and that the hydrogen and oxygen are present in the proportion of two atoms of the former to one atom of the latter. Since this is the proportion in which hydrogen and oxygen combine to form water, it was thought that the compounds belonging to this group are compounds of carbon with water, and the name *carbohydrate* was applied to them. The name is still retained, but the assumption on which it was based is no longer accepted.

**Sugars.**—Speaking generally, the sugars are crystalline substances which are soluble in water and have a sweet taste. The most important sugars have a composition represented either by the formula  $C_6H_{12}O_6$ , or by the formula  $C_{12}H_{22}O_{11}$ . To the former group, known as the *monosaccharides*, belong the sugars *glucose* and *fructose*, which are found in the juice of ripe fruits and in honey; while to the latter group, known as the *disaccharides*, there belong: *sucrose*, which is present in the juice of the sugar cane and of the sugar beet; *lactose*, which occurs in the milk of mammals; and *maltose*, which is formed in malt by the action of diastase on starch. Whereas all these compounds contain a number of alcoholic hydroxyl groups, and therefore behave chemically like alcohols, glucose contains also an aldehydic group and fructose a ketonic group. These simpler sugars have reducing properties and cause silver to separate out from an ammoniacal solution of silver oxide (p. 398).

Under the catalytic action of dilute acids or of enzymes, sugars of the formula,  $C_{12}H_{22}O_{11}$ , undergo hydrolysis in aqueous solution and yield sugars of the formula  $C_6H_{12}O_6$ . Cane sugar, for example, yields a mixture of glucose and fructose, the mixture being known as *invert sugar*. The process of hydrolysis is in this case spoken of as *inversion*.

**Starch.**—Starch is one of the most important products of plant life, and the most abundant of foods. In the form of minute, colourless granules which, under the microscope, exhibit a zoned structure (Fig. 81), and which differ in appearance according to their source, starch is stored by plants in the seeds of cereals and in the tubers of plants like the potato. From these, the starch can be obtained by crushing or rubbing in water and running the milky liquid through fine sieves. The starch granules are allowed to settle

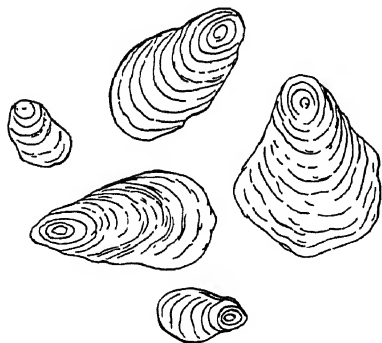


FIG. 81.—Starch grains under the microscope.

and are then separated to a large extent from water by centrifuging.

Starch is insoluble in cold water, but when warmed with water the granules burst and form an opalescent, colloidal sol which, if sufficiently concentrated, sets to a jelly or paste on cooling. With even a small quantity of iodine, starch gives a

material of a deep-blue colour. On being boiled with dilute acids, starch undergoes hydrolysis and forms glucose.

Starch may be represented by the formula,  $(C_6H_{10}O_5)_n$ , but the value of the molecular weight and therefore of  $n$  is not known.

**Cellulose.**—One of the most important, as it is the most abundant of plant products, cellulose forms the essential constituent of the woody fibre and skeletal framework which support the living and growing cells of plants; and it has become the basis of many of the most important industries in our present-day civilisation. Many different plants, flax, cotton, etc., are cultivated specially for its production.

When cellulose is heated under pressure with dilute acid, hydrolysis takes place and the sugar, glucose, is formed. By this means, wood waste may be used as a source of glucose for the production of alcohol.

**Paper.**—The growth of civilisation is intimately bound up with the arts of writing and printing, with the preserving of accurate records and the transmission of ideas. To the Egyptian papyrus there succeeded paper, which was first made by the Chinese, even before the beginning of the Christian era, from cotton and other vegetable fibres. Until about a century ago, paper continued to be made entirely from cotton and linen rags, but, during last century, the supply of these became inadequate, and recourse was had, therefore, to straw, grasses (*e.g.* Esparto grass) and other less pure forms of cellulose. Of the different sources of cellulose used at the present day for the manufacture of paper, wood is by far the most important; and the great timber-growing countries, Scandinavia and Canada, furnish most of the cellulose required for this purpose.

Wood fibre consists mainly of a compound of cellulose with lignone, encrusted frequently with resinous matter, and in order to isolate the cellulose, this compound must be decomposed. This is now mostly done by boiling the wood, in the form of shavings or chips, with a solution of calcium bisulphite,<sup>1</sup> the wood being boiled with the liquor under a pressure of several atmospheres. Not only is the wood fibre thereby chemically broken up, with production of cellulose, but the latter is also bleached to some extent by the sulphite. The cellulose is now separated from the sulphite liquor, washed and beaten with water so as to break down the fibres into small shreds, and in this form it constitutes wood pulp ("sulphite pulp")

For the manufacture of paper, the fine cellulose fibres obtained

<sup>1</sup> This substance,  $Ca(HSO_3)_2$ , is formed by the action of sulphurous acid solution of sulphur dioxide in water) on limestone.

from the disintegrated cotton rags, grass or wood pulp, are bleached, washed and mixed with colouring matters if desired. They are then suspended in water and run over an endless band of wire gauze, through which the water drains away, and the fibres are caused to felt together by giving a vibratory motion to the band of gauze. The web of felted pulp is now carried between heated rollers whereby the paper is dried.

The paper so obtained is loose in texture and of the nature of blotting paper; and to make it suitable for writing it must be sized. For this purpose it is passed through solutions of alum and of rosin soap, whereby a compound of rosin and aluminium is formed, which binds the fibres together and prevents the ink from running. The addition of the sizing materials may, if desired, be made to the pulp before making into paper. Very frequently, also, powdered gypsum, white clay or similar substances are added to the paper pulp in order to "load" or give body to the paper, fill up its pores and allow of a more highly glazed surface being obtained by calendering, or rolling with hot rollers.

**Rayon (Artificial Silk).**—In the year 1889, there was exhibited in Paris a material which, in its general appearance, imitated in a remarkable manner the fibre spun from the glands of the silkworm. This material, however, invented by the French chemist, COUNT HILAIRE DE CHARDONNET, was not silk, nor was it derived from any animal source whatever, but from the vegetable material cellulose.<sup>1</sup>

Nitro-cellulose, or, more correctly, cellulose nitrate, dissolves, as we have seen, in a mixture of alcohol and ether, and when the viscous liquid so obtained is forced under pressure through fine capillary jets, and the solvents evaporated off by means of warm air, thin filaments are obtained which are then spun into thread and twisted into yarn. By treating the yarn with a solution of ammonium sulphide or sodium sulphide, the nitrate groups, to the presence of which the cellulose nitrate owes its inflammable and explosive properties, are removed, and there is again obtained what is practically cellulose. The twisted structure of the natural fibre, however, has given place to a smooth cylindrical filament which has all the superficial appearance and lustre of silk.

It was not long before other and better methods of transforming cellulose into threads resembling silk were invented; and the method by which most of the artificial silk, or *rayon*

<sup>1</sup> True silk belongs to a class of substances known as proteins, and contains nitrogen as well as carbon, hydrogen and oxygen.

as it is now generally called, is made at the present day, was invented by the two English consulting chemists, CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN. According to this process, cellulose is converted into a thick syrup-like material known as *viscose*, by successive treatment with caustic soda and carbon disulphide, and the syrup-like viscose, consisting essentially of a compound known as cellulose sodium xanthate, is forced through fine jets into a bath containing sulphuric acid and other substances. Thereby, the viscose filament is coagulated and converted into lustrous, silk-like filaments of cellulose.

When the viscose is kept for some days, it undergoes spontaneous decomposition with production of a hard, horn-like material, known as *cellophane*. Transparent and non-inflammable films can also be obtained by spreading viscose on glass at a temperature of about 60° C. Thin sheets of cellophane are now much used for wrapping food and other materials, and also, by druggists, as caps for bottles. Placed in position while wet, it shrinks greatly on drying and so fits tightly to the bottle.

Another kind of artificial silk is also produced under the names of *celanese* and *lustron*. This material does not consist merely of transformed cellulose, but is a compound (an ester) of cellulose and acetic acid, that is, *cellulose acetate*. A viscous solution of this compound in acetone is forced through jets, and the issuing filaments are coagulated by evaporation of the acetone by means of warm air.

The artificial silks just described must not be confused with the lustrous material known as *mercerised cotton*, so called after JOHN MERCER, an English calico printer, who, in 1844, found that when cotton is acted on by a solution of caustic soda, the naturally flat, twisted fibres swell to a cylindrical form and become shorter. Forty-five years later, in 1889, H. A. LOWE discovered that when the cotton fibres are tightly stretched during their treatment with caustic soda solution, so that they cannot shrink, they exhibit, after washing and drying, a silky lustre, due to the reflexion of light from the smooth surface of the fibre.

**Celluloid.**—In 1869, the brothers HYATT, of Albany, N.Y., found that if camphor is added to a mixture of nitro-cotton and alcohol, a hard, horn-like material is obtained, which can readily be fashioned, while hot, into articles of various shapes and forms. To this material the name *celluloid* was given. Although naturally of a clear gelatin-like appearance, celluloid can easily be dyed, and can, by suitable treatment, be made to imitate not only such materials as bone and ivory, but also amber, tortoise-

shell, marble and agate. Light in weight and not readily breakable, celluloid is used for the manufacture of photographic films and for many small articles of common use. It is, however, a material the use of which is not altogether free from danger since the basis of celluloid is the highly inflammable cellulose nitrate. The acetate of cellulose, however, when mixed with camphor or suitable substitutes, yields a material, called *cellon*, which resembles and is even superior to celluloid in its general properties, and is not inflammable. It is used for the manufacture of non-inflammable cinematograph films, for making the bristles of hair-brushes, etc. In the form of a thick viscous solution it is employed as a flexible varnish for wood, paper and metal, for enamelling aeroplanes, etc.

**Imitation Leather and Lacquers.**—If nitro-cellulose is mixed with a drying oil, such as linseed oil, and with colouring matters, and the mixture spread on fabric, a sort of “oil-cloth” is obtained; and on passing this between suitably cut rollers, the material is grained and a very good imitation leather, *e.g.* rexine, is produced.

At the present day, nitro-cellulose is also very extensively employed for the preparation of lacquers and enamels, which are much used for the finishing of motor-car bodies, etc. For the production of such lacquers, the nitro-cellulose is dissolved in a suitable solvent, and to the solution there are added a quantity of gum or resin, a plasticiser (in order to prevent the film from becoming brittle) and a pigment. After application, the lacquer rapidly dries, and the film so obtained is characterised by its hardness, toughness and resistance to scratching and rubbing.

## CHAPTER XXVIII

### STEREOCHEMISTRY

By the introduction of the doctrine of valency and of the Kekulé-Couper diagrammatic method of representing molecular constitution, a satisfactory basis seemed to have been obtained for the future development of organic chemistry. And yet, it was not long before the insufficiency of this theory of chemical structure became only too apparent, owing to the discovery that, in some cases, the number of isomeric compounds is greater than can be represented by the structural formulæ of Kekulé. A new isomerism was discovered, an isomerism which manifested itself in the property known as *optical activity*.

Early last century it was discovered that when a ray of light is passed through a crystal of Iceland spar, the ethereal vibrations, which propagate the light, and which, ordinarily, take place in all directions at right angles to the path of the ray, are all brought into one plane. The light is said to be *polarised*. When, now, this polarised light is passed through certain substances, quartz, turpentine, a solution of cane sugar, etc., it is found that the plane of polarisation, the plane in which the ethereal vibrations take place, is rotated or twisted, this rotation or twisting taking place sometimes to the right, sometimes to the left; an effect which one can illustrate by twisting a strip of stout paper into a right-handed or left-handed spiral, such as is represented in Fig. 82. Substances which possess this property of rotating the plane of polarised light, are said to be "optically active."

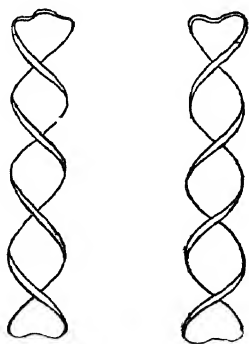


FIG. 82.—Right and left-handed spirals.

This property of optical activity can also be demonstrated by a modification of a very interesting experiment due to the English physicist, Sir GEORGE GABRIEL STOKES (1819-1903). When a beam of light from a projection lantern (Fig. 83) is

reflected vertically downwards by means of a mirror, through a column of water rendered slightly turbid by the addition of a few drops of an alcoholic solution of rosin, the path of the beam is rendered visible by the fine suspension of rosin particles (Tyndall phenomenon, p. 402); and the beam of light appears equally bright all round. But if the light from the lantern is first polarised by passage through a prism of Iceland spar, and then reflected downwards through the column of water, the appearance obtained is that of a band which is light *only on two* opposed sides, and dark on the other two opposed sides. On rotating the prism of Iceland spar, the band also rotates and turns alternately its light and dark sides to the eye. The effect produced is as if the beam of light on passing through the prism of Iceland

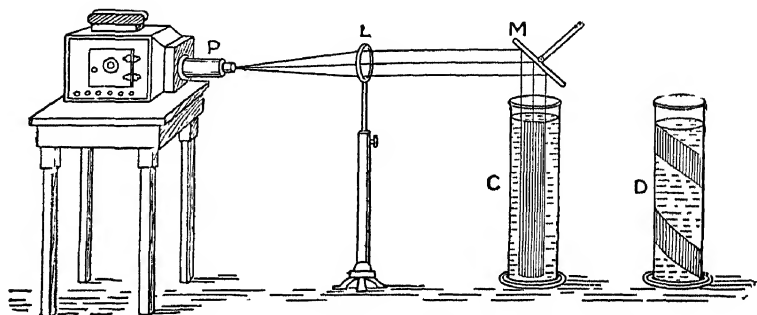


FIG. 83.—Demonstration of the polarisation of light.

Light from a lantern is polarised by passage through the polarising prism P, and the beam of light is then directed by the lens L on to a mirror M, by which the light is directed vertically downwards through water contained in the cylinder C, and rendered turbid by a fine suspension of rosin. A vertical, polarised band of light is obtained. If the cylinder C is replaced by D, which contains a concentrated solution of cane sugar, the band of light is twisted into the form of a spiral.

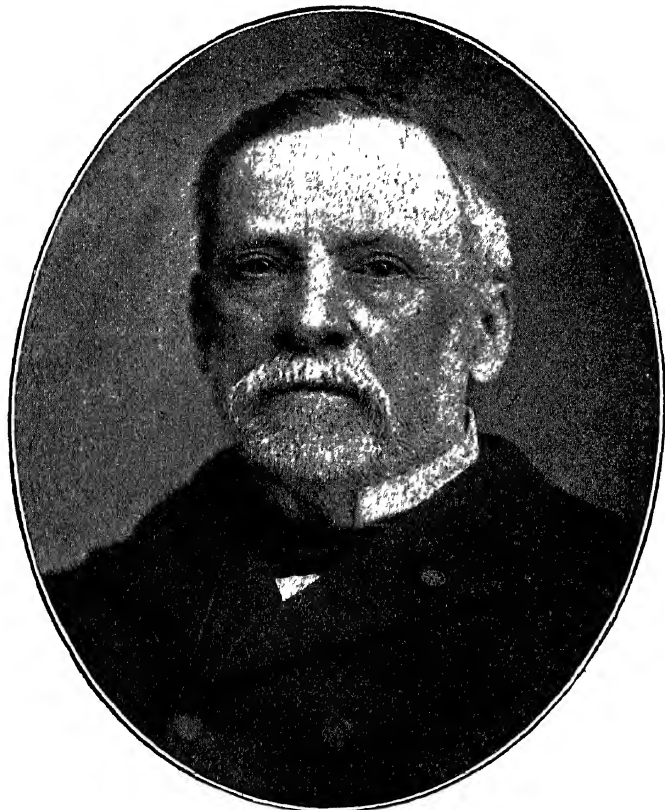
spar were given a flat form, like a book, from the two opposite edges of which light is emitted, while the sides remain dark. Thus we have illustrated the phenomenon of polarisation of light. If, now, the cylinder of water is replaced by a cylinder containing a solution of cane sugar, the band of light is twisted into a spiral form, and on rotating the prism of Iceland-spar, this spiral band of light will appear to move with a screw-like motion. From the fact that the different rays of coloured light which together constitute white light, are twisted or rotated to different extents (the blue rays being rotated more than the red), the spiral band of light shows the colours of the rainbow.

The study of this remarkable property of substances of rotating the plane of polarised light, a property which has occupied the attention of many chemists down to the present



day, was inaugurated by the brilliant discoveries of PASTEUR in 1848.

LOUIS PASTEUR, son of a tanner who was also "ancien militaire sous le Premier Empire, Chevalier de la Légion d'Honneur,"<sup>1</sup> was born at Dôle, in the Jura, on 27th December, 1822. After receiving his early education at the Collège Communal at



LOUIS PASTEUR.

Arbois, whither his father had removed, and after graduating at the University of Besançon, Pasteur, in 1843, entered the École Normale at Paris. Here he studied chemistry under Balard, the discoverer of bromine, and also attended the lectures of Dumas at the Sorbonne. On the completion of his course at the École Normale, Pasteur was retained as Balard's assistant, and, his interest having been aroused in crystallography, he

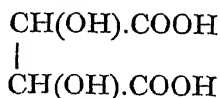
<sup>1</sup> From Pasteur's dedication to the memory of his father of his book, *Études sur la Bière*.

commenced the investigations of the crystals of tartaric acid and the tartrates, which were to inaugurate a new chapter in organic chemistry and which will be discussed in the following pages.

After serving for three months as Professor of Physics at the Lycée at Dijon, Pasteur, in 1848, became Deputy-Professor and, in 1852, Professor of Chemistry in the University of Strasbourg. In 1854, he was transferred to Lille and, in 1857, to the École Normale at Paris. It was at Lille that Pasteur, forsaking his first more purely chemical investigations which, however, formed the basis of his future extraordinary achievements, took up the serious study of the processes of fermentation, and so began that long and impressive series of bio-chemical and bacteriological investigations which constitute one of the greatest monuments in the history of science and which, in their applications, have proved of inestimable benefit to industry and humanity. Not only was it by the work of Pasteur that the silk-worm disease, *pébrine*, was successfully combated and the silk cultivation of France, Spain and Italy saved from extinction, but it is to Pasteur that much of the present-day prosperity of the various fermentation industries is due. It is to Pasteur, also, that we owe our earliest knowledge of the bacterial origin of disease and the production of immunity by vaccines, which led to the culminating glory of Pasteur's life, the cure of rabies or hydrophobia. It is, moreover, on the foundations of Pasteur's work that the practice of antiseptic surgery was built up, whereby the havoc and torture of festering sores and gangrenous wounds were abolished from the surgical wards of our hospitals. No more glorious life of service to humanity, surely, has ever been achieved by any man of science.

Pasteur died on 28th September, 1895, and his body rests in the crypt of the *Institut Pasteur*, which was erected in 1888 as a tribute to his genius and in gratitude for the services which he had rendered to mankind.

When Pasteur commenced the investigations which were to initiate a revolution in the current ideas regarding the molecular structure of organic compounds, two isomeric acids were known having the same composition, namely, tartaric acid and paratar-taric acid. The structure of these two acids is the same and is represented by the formula



The former acid, which is found occurring in grape juice, is optically active; the latter is inactive. On examining the crystals of these two acids, and of a number of their salts, Pasteur found that whereas the crystalline faces of the inactive paratartaric acid and its salts were all fully developed, and the crystals symmetrical (Fig. 84), in the case of the active tartaric acid, the full development of the crystalline faces was interrupted by the occurrence of so-called hemihedral faces (Fig. 85). The occurrence of these hemihedral faces was regarded by Pasteur as the outward and visible manifestation of the property of optical activity, in accordance with a view which had been suggested in 1820 by Sir JOHN F. W. HERSCHEL (1792–1871) in the case of crystalline quartz, which is also optically active. But whereas quartz is optically active only in the crystalline state, tartaric acid retains the property even when dissolved. In the

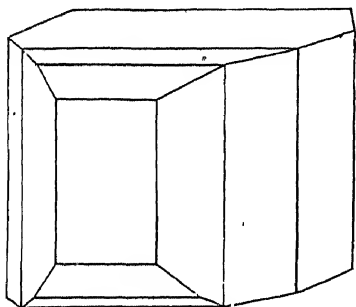


FIG. 84.—Holohedral crystal of paratartaric acid.

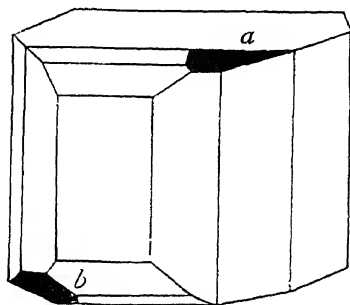


FIG. 85.—Crystal showing hemihedral faces, *a* and *b*.

former case, the property depends on the crystalline structure; in the latter, it depends on the internal molecular structure.

A further discovery was made by Pasteur. During his investigation of one of the salts of tartaric and paratartaric acid (namely, sodium ammonium tartrate and sodium ammonium paratartrate), Pasteur found, as was to be expected, that the crystals of the tartrate resembled those of the other tartrates he had examined, in possessing hemihedral faces arranged in a similar manner. The crystals obtained from the solution of the paratartrate, however, instead of being holohedral, with the crystalline faces fully developed, were found also to have hemihedral faces; but these hemihedral faces, instead of, as in the tartrates, all being turned the same way, were inclined, sometimes to the right and sometimes to the left (Fig. 86). This result was quite unexpected; and Pasteur, on carefully separating the two sets of crystals and examining their solutions, discovered,

with no less surprise than pleasure, that one set of crystals rotated the plane of polarised light to the right, while the other set rotated the plane by an equal amount to the left. On dissolving together equal amounts of the two sets of crystals, a solution was obtained which was quite inactive.

Here, then, we have the discovery of that new kind of isomerism to which reference has just been made, and which showed the insufficiency of the structural formulæ of Kekulé. The two salts into which the paratartrate had been separated by crystallisation were identical in all their chemical and physical properties, save only in the disposition, to the right or to the left, of the small hemihedral faces occurring on their crystals, and in the property of rotating the plane of polarised light to an equal extent but in opposite directions. From these two salts, Pasteur obtained two different tartaric acids: one having the power of

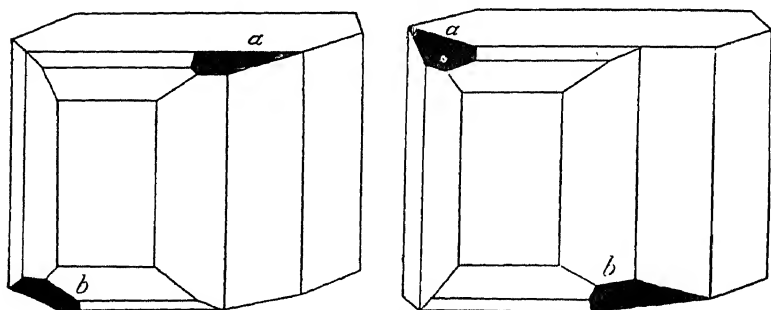


FIG. 86.—Enantiomorphic crystals of optically active tartrates.

rotating the plane of polarised light to the right and identical with the acid occurring in grape juice, the other hitherto unknown, and having the power of rotating the plane of polarised light to the left. Moreover, on mixing together in solution equal quantities of these two optically active acids, there separate from the solution crystals of the inactive paratartronic acid, which is thus shown to be a compound of the two active acids in equal proportion.

The discovery of the two optically active tartaric acids was a momentous one, effecting a revolution in the views of chemists regarding molecular structure; and we can well understand the feeling of happiness and the nervous excitement by which Pasteur was overcome on making the discovery. Rushing from his laboratory and meeting the lecture-assistant (*préparateur*) in physics, he embraced him, exclaiming: "I have just made a great discovery! I have separated the sodium ammonium paratartrate

into two salts of opposite action on the plane of polarisation of light. The dextro-salt is in all respects identical with the dextro-tartrate. I am so happy and overcome by such nervous excitement that I am unable to place my eye again to the polarisation apparatus." The question, however, now arose as to how the existence of the two optically active tartaric acids could be explained.

All material things belong to one or other of two classes, according as the image of the object which is formed in a mirror, is such that it can or cannot be superposed on the object. In the case of a cube, for example, the image formed in a mirror is identical with the object, and we can imagine the image superposed on the original cube. A cube is a symmetrical object. But if a right hand is held in front of a mirror, the image which is obtained represents a left hand, and this cannot be superposed on the right hand; a right hand will not fit into a left-hand glove. In the case of a hand, therefore, we have an asymmetrical object, which can exist in two distinct, so-called *enantiomorphic* forms, similar in all respects, but not superposable, not identical. And when we examine the crystals of the two optically active tartaric acids (or of their salts), it is seen that they also are related to each other as the right hand is to the left hand; each represents the non-superposable mirror image of the other (Fig. 86), and the two crystals, although in all points similar, are not identical. If, however, the crystalline form is to be regarded, as Pasteur regarded it, as a visible manifestation of the internal structure, we are led to the conclusion that the *molecular* structures of the two active tartaric acids are asymmetric and enantiomorphously related to each other as object to non-superposable mirror image.

Although Pasteur did not develop his views into a theory of chemical structure, he introduced into chemistry a conception of extraordinary importance and fruitfulness, the conception of *molecular asymmetry*, and he recognised that molecular structure is not a matter of two dimensions only, but of three. The atoms are not arranged in a plane, as the formulæ of Kekulé represent them, but in three-dimensional space. In this way Pasteur inaugurated a new chemistry, a "Chemistry in Space" or "Stereo-Chemistry."

The conception of molecular asymmetry and the idea of the grouping of the atoms at the corners of a tetrahedron were developed independently, in 1874, into a consistent theory of molecular structure, embracing the optically active isomeric compounds, by the Dutch chemist, VAN'T HOFF, and the French chemist, JOSEPH ACHILLE LE BEL.

If we imagine a carbon atom at the centre of a tetrahedron, and if the four atoms or groups, with which, as we have seen, a carbon atom can be united, are situated at the four corners of the tetrahedron, it will be found that so long as two, at least, of the atoms or groups are the same, the molecule, represented as a tetrahedron, will be symmetrical and its mirror image will be superposable on and therefore identical with the original. This will be clear from an inspection of Fig. 87, which represents

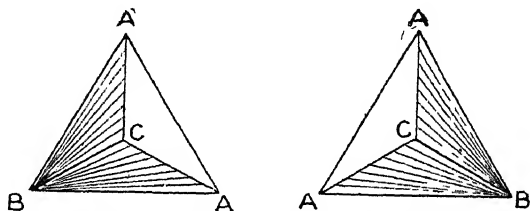


FIG. 87.—Symmetrical tetrahedron and its mirror image.

such a tetrahedron and its mirror image. The right-hand tetrahedron, obviously, only requires to be turned through an angle of rather more than  $90^\circ$ , on the corner, B, as a pivot, to become identical in disposition with the left-hand tetrahedron.

If, however, the four atoms or groups attached to the carbon atom are all different, the molecule, as represented by the tetrahedron, becomes asymmetric, and gives a mirror image which is

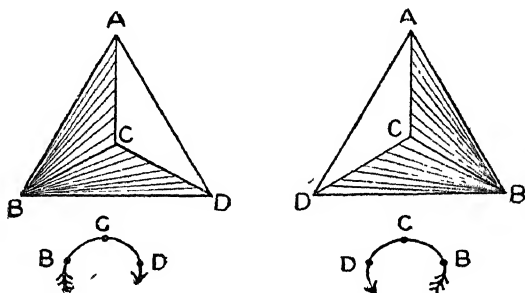


FIG. 88.—Asymmetric tetrahedron and its mirror image.

no longer superposable on the original. Two isomeric forms are therefore possible. This will be understood from Fig. 88. Viewing these tetrahedra from a similar position, we see that the groups B C D., in the one case, are arranged from left to right ; in the other case, from right to left. If one of these represents a molecule which rotates the plane of polarised light to the right, the other will represent a molecule which rotates the plane of polarised light to the left.

The views of van't Hoff and Le Bel have received the amplest confirmation. Not only has it been found that all compounds which are optically active do contain at least one atom of carbon to which four different atoms or groups are attached—a so-called *asymmetric carbon atom*—but also, no compound has been obtained the possible existence of which could not be predicted by means of the van't Hoff and Le Bel theory.<sup>1</sup> So fruitful has the conception of molecular asymmetry and of the asymmetric carbon atom proved, that it has been extended also to the atoms of other elements than carbon, of which optically active isomers have been prepared.

We have already seen that in the case of tartaric acid—and the same holds in all other cases of optically active substances—there exist, or can exist, not only the two optically active isomers, but also an inactive isomer, produced by the combination of the two oppositely active forms in equal amounts, and separable again, by suitable means, into the active forms. This inactive form is known as the *racemic* form. Besides the three isomeric forms just referred to, there exist, in the case of compounds which contain more than one asymmetric carbon atom, other isomers which are optically inactive but which cannot be resolved into the optically active forms.

<sup>1</sup> Optical activity is also found even when no asymmetric carbon atom is present, provided the structure of the molecule as a whole is asymmetric.

## CHAPTER XXIX

### THE AROMATIC COMPOUNDS

THE aromatic compounds, so-called because most of the naturally-occurring members of this group form the aromatic or fragrant constituents of essential oils, spices and balsams, constitute by far the largest group of organic compounds; and just as the aliphatic compounds may be regarded as derived from methane, so the aromatic compounds may be regarded as derived from the hydrocarbon benzene. Although this substance was discovered by Faraday as early as 1825, it was not till 1865, as we have seen, that its *constitution* was unravelled by Kekulé; and not until the constitution of benzene was known was it possible to develop effectively the chemistry of the aromatic compounds.

The main source of benzene and of many of its most important derivatives is the thick, oily, dark-coloured *coal-tar* which is obtained, as has already been pointed out (p. 197), when bituminous coal is distilled in closed retorts at a temperature of 1000°–1200° C.

**Coal-tar** is an exceedingly complex mixture of over two hundred different compounds, some of which, however, are present only in very small amount. The separation and isolation of all these different substances is not attempted, but by subjecting the crude coal-tar to a process of distillation, various "fractions" are obtained. First of all, while the temperature of the still gradually rises to 170° C., there distils over what is known as "light oil." This is followed, between the temperatures of 170° and 230°, by the "carbolic oils," and between 230° and 270°, by the "creosote oils." Lastly, between 270° and 400°, there pass over the "anthracene oils," and a residue of pitch, a valuable material used in road-making, is left in the still.

The crude coal-tar having in this way been separated into a number of different portions, each of these portions is then subjected to suitable chemical treatment and to repeated distillation in order to effect a more complete separation into the different constituents. Thus the light oil is separated into "crude benzole"—consisting of a mixture of the hydrocarbons,



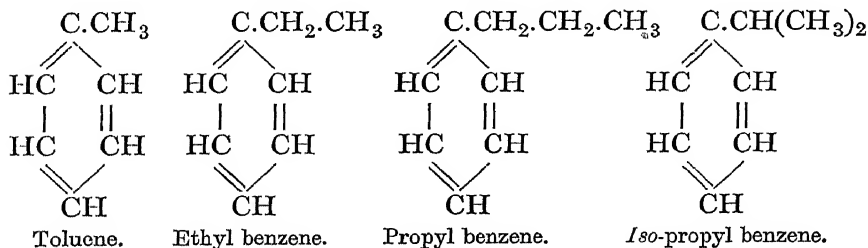
benzene, toluene and xylene—"solvent naphtha" and "burning naphtha," consisting of xylene and other higher hydrocarbons. To obtain pure benzene and toluene, such as are required in the manufacture of dyes, drugs, explosives, etc., the crude benzole is "rectified" by distillation in a special still.

The portion of the tar distillate known as "carbolic oils" or "middle oils" is likewise separated by chemical and physical treatment into its chief constituents. As the distillate cools down, there crystallises out from it the hydrocarbon known as naphthalene; and the residual oil, known as "crude carbolic oil"—consisting especially of carbolic acid or "phenol" and of three isomeric compounds known as cresols—is used for the manufacture of disinfectants.

Although the amounts of the different compounds obtained vary with the nature of the tar and the treatment to which it is subjected, the quantities of the more important constituents yielded by one ton of tar are approximately as follows:

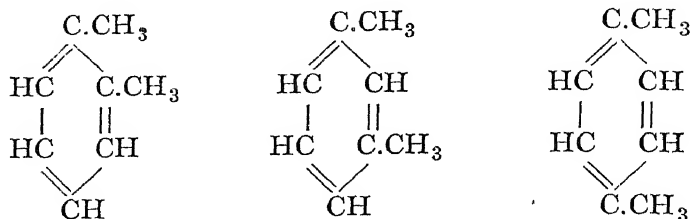
Benzene and toluene . . . . .	25 lbs.
Phenol . . . . .	11 "
Cresols . . . . .	50 "
Naphthalene . . . . .	180 "
Anthracene . . . . .	6 "

**Homology and Isomerism.**—In the case of the aromatic as in the case of the aliphatic group, the compounds can be arranged in various homologous series, which can be regarded as derived from the parent hydrocarbon benzene. Thus, by replacing one of the hydrogen atoms of the benzene molecule by the group  $\text{CH}_3$ .,  $\text{C}_2\text{H}_5$ .,  $\text{C}_3\text{H}_7$ ., etc., a homologous series of hydrocarbons can be built up— $\text{C}_6\text{H}_5\cdot\text{CH}_3$ ,  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_7$ , etc.—the structure of which would be represented by the formulæ,



These hydrocarbons will, of course, exhibit the same sort of isomerism as is found in the hydrocarbons of the methane series. But a further possibility of isomerism exists in the case of the benzene series, owing to the fact that more than one of the benzene hydrogen atoms may be replaced by hydrocarbon radicals, and

the properties of the compounds obtained will depend on the *relative position* of the substituting groups in the benzene ring. Thus, if two hydrogen atoms of the benzene ring or "nucleus," as it is also called, are replaced by  $\text{CH}_3$ -groups, three isomeric hydrocarbons are obtained, represented by the formulæ,



and called respectively, *ortho*-xylene, *meta*-xylene and *para*-xylene, the terms *ortho*, *meta* and *para* indicating the relative positions of the two methyl radicals. This type of isomerism is of very great importance in the case of the aromatic compounds.

It will, of course, be noticed that the three xylenes are also isomeric with ethyl benzene,  $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_3$ .

Owing to the existence of position isomerism in the benzene ring, it will be readily understood that in the case of the homologous series of aromatic compounds, the possibilities of isomerism are very much greater than in the case of the aliphatic compounds.

**Benzene and its Homologues.**—In 1815, there was introduced by the Portable Gas Co., London, an illuminating gas, obtained by the decomposition by heat of fish oils, and this gas was supplied to the consumers in cylinders into which it had been pumped under a pressure of thirty atmospheres. Under this pressure, a portion of the gas condensed to a liquid, and from this liquid FARADAY, in 1825, isolated a compound, the composition of which he found to be represented by the empirical formula  $\text{CH}$ , and which he called bi-carburet of hydrogen. Some nine years later, however, the compound was rechristened by LIEBIG, who gave to it the name *benzol*—a name which it still bears in Germany.<sup>1</sup> This name, formed by a contraction of *benzoin c eum*, was suggested by the fact that, as had just been discovered, the hydrocarbon can be obtained by heating benzoic acid,  $\text{C}_6\text{H}_5.\text{COOH}$ , with lime. Benzoic acid, in turn, was obtained by the dry distillation of the fragrant resin, known from a very early time and called by the Arabs, *lubān jāwī*, or the

<sup>1</sup> In England, the term *benzol* or *benzole* is applied to various commercial mixtures of benzene hydrocarbons.

frankincense of Java.<sup>1</sup> By a succession of corruptions, this name passed into English as *Benjamin* and *benzoin*, the resin being now called *gum benzoin*. For the sake of uniformity in the nomenclature of hydrocarbons, the name benzol was later changed to benzene. That benzene is present as a constituent of coal-tar was discovered in 1845 by AUGUST WILHELM VON HOFMANN (1818–1892), at that time Professor in the Royal College of Chemistry, London.

*Benzene* is a colourless volatile liquid which yields a readily inflammable vapour. Owing to the fact that the compound contains a high proportion of carbon, benzene vapour burns with a luminous and smoky flame. Mixed with alcohol or with gasoline (petrol), it is largely used as a fuel for automobile engines, especially on account of its valuable "anti-knock" properties.

*Toluene*,  $C_6H_5.CH_3$ , a hydrocarbon similar in properties to benzene, is valuable mainly as a raw material for the synthesis of a number of important compounds. By the action on it of a mixture of nitric and sulphuric acids, there is obtained the explosive compound *trinitrotoluene* (T.N.T.).

By the action of a mixture of nitric and sulphuric acids on benzene, there is obtained nitrobenzene ( $C_6H_5.NO_2$ ), a substance used under the name of *essence of mirbane* as a substitute for oil of bitter almonds. When this compound is shaken with iron filings in presence of dilute hydrochloric acid, the hydrogen formed by the action of the iron on the acid reduces the nitrobenzene to *aniline*,  $C_6H_5.NH_2$ , a liquid which boils at  $183^\circ C$ . This compound, one of the most important members of the aromatic group and one which has played a part of great importance in the history of synthetic dyes and drugs, owes its name to the fact that it was first obtained by the distillation of indigo—the word aniline being derived from *anil*,<sup>2</sup> an old name for indigo.

**Phenols.**—The term *phenol* is applied to those derivatives of benzene in which one or more of the hydrogen atoms attached to the benzene ring have been replaced by the hydroxyl group. The name is applied more specifically to the first known and most important member of the group, *carbolic acid*,<sup>3</sup>  $C_6H_5.OH$ , first discovered in coal-tar.

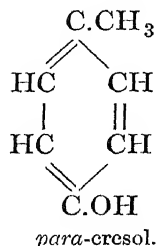
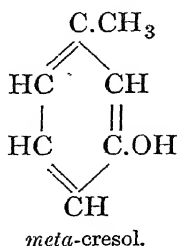
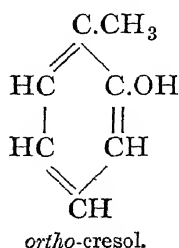
Pure phenol is a white crystalline solid which melts at  $42^\circ C$ . It dissolves to some extent in water and the solution is used as

<sup>1</sup> The resin was really obtained from Sumatra.

<sup>2</sup> Derived from the Arabic *al-nil* or *an-nil*, the blue substance.

<sup>3</sup> From *carbo*, coal, and *oleum*, oil.

a disinfectant and antiseptic. For this purpose, however, it is now largely displaced by its homologues, the *cresols*, which occur in coal-tar in three isomeric forms, represented by the formulæ,

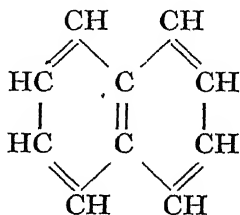


These compounds not only have a greater germicidal action but they are also less poisonous than phenol, and are now widely used as disinfectants. *Lysol*, for example, consists essentially of a mixture of cresols with a potash soap and a small amount of glycerin. The soap, as we have seen (p. 235), enables the cresols to mix homogeneously with water at the ordinary temperature. The cresols, also, form the essential constituent of *Jeyes' Fluid*, *Cresolin*, and other disinfectants.

On being nitrated, phenol yields, as we have seen, the important explosive *picric acid*,  $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$ .

**Naphthalene and Anthracene.**—Naphthalene, as has been pointed out, separates out from the "middle oil" fraction of coal-tar, and, when purified, forms a white crystalline solid with a characteristic smell. Apart from its important uses in chemical industry, naphthalene is employed mainly as a disinfectant and as a preservative of furs, etc., against the attack of moths and other insects.

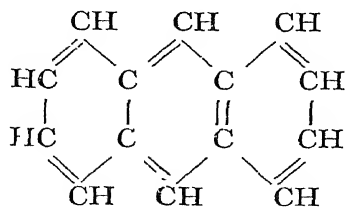
Naphthalene is a hydrocarbon having the composition  $\text{C}_{10}\text{H}_8$ , its structure being represented by the formula,



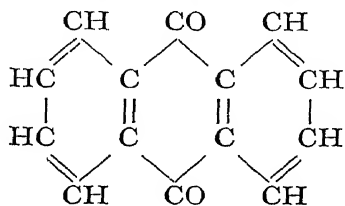
Naphthalene is the starting material in the synthesis of the dye-stuff, indigotin.

**Anthracene**,  $\text{C}_{14}\text{H}_{10}$ , occurs in only comparatively small

amount in coal-tar. Its molecular structure is that of three benzene rings joined together as shown by the formula,



When anthracene is oxidised it passes into *anthraquinone*,



This is the parent substance of alizarin and of many other important dyes.

While the importance of the aliphatic compounds—the fats, carbohydrates, proteins, etc.—lies largely in their occurrence as natural products of inestimable biochemical significance, the aromatic compounds, which are, for the most part, products of the laboratory, command our admiration and claim our interest mainly as triumphs of the human intellect, and as materials of great industrial value. From about half a dozen of the compounds isolated from coal-tar, chemists have succeeded in building up or synthesising a vast array of compounds—dyes, drugs, photographic chemicals, perfumes, etc.—the production of which has not only given rise to industries of great national importance, but has profoundly influenced the development and progress of civilisation.

## APPENDIX I

### LIST OF BOOKS FOR FURTHER READING

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A. D. RITCHIE. *Scientific Method.* London: Kegan Paul, Trench, Trubner & Co.

#### CHAPTER II

- J. H. BREASTED. *History of Egypt.* London: Hodder & Stoughton.  
A. LUCAS. *Ancient Egyptian Materials.* London: Arnold & Co.  
J. E. MERCER. *Alchemy Its Science and Romance* London: Society for the Promotion of Christian Knowledge.  
J. M. STILLMAN. *The Story of Early Chemistry.* New York: D. Appleton & Co.  
J. MOORE. *A History of Chemistry.* New York: McGraw-Hill Book Co.  
E. J. HOLMYARD. *Chemistry to the Time of Dalton.* Oxford University Press.

#### CHAPTER III

- R. BOYLE. *The Sceptical Chymist.*  
W. A. TILDEN. *Famous Chemists, Chap. I.* London: Routledge & Son; New York: E. P. Dutton & Co.  
J. I. O. MASSON. *Three Centuries of Chemistry.* London: Ernest Benn, Ltd.  
T. E. THORPE. *Essays in Historical Chemistry, Chap. 1.* London: Macmillan & Co.

#### CHAPTERS IV AND V

- IDA FREUND. *The Study of Chemical Composition.* Cambridge University Press.  
J. A. V. BUTLER. *The Chemical Elements and their Compounds.* London: Macmillan & Co.  
R. M. CAVEN and J. A. CRANSTON. *Symbols and Formulæ in Chemistry.* London: Blackie & Son.  
W. A. TILDEN. *Famous Chemists, Chaps. VI and XIX.* London: Routledge & Son; New York: E. P. Dutton & Co.

## CHAPTER VI

- F. SODDY. The Interpretation of Radium. London: John Murray.  
E. N. DA C. ANDRADE. Structure of the Atom. London: G. Bell & Sons.  
G. P. THOMSON. The Atom. London: Thornton Butterworth.  
F. W. ASTON. Isotopes. London: Arnold & Co.  
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## CHAPTER VII

- J. PERRIN. Atoms. Trans. by D. Ll. Hammick. London: Constable & Co.

## CHAPTER VIII

- W. L. HARDIN. The Rise and Development of the Liquefaction of Gases. London: Macmillan & Co.  
W. H. BRAGG and W. L. BRAGG. X-rays and Crystal Structure. London: G. Bell & Sons.

## CHAPTER IX

- IDA FREUND. The Study of Chemical Composition. Cambridge University Press.

## CHAPTER X

- W. RAMSAY. The Gases of the Atmosphere. London: Macmillan & Co.  
CLARA M. TAYLOR. The Discovery of the Nature of the Air. London: G. Bell & Sons.  
M. W. TRAVERS. The Discovery of the Rare Gases. London: Arnold & Co.  
T. E. THORPE. Joseph Priestley. London: Dent & Co.; New York: E. P. Dutton & Co.  
W. A. TILDEN. Sir William Ramsay. London: Macmillan & Co.  
C. W. SCHEELÉ. The Discovery of Oxygen (Alembic Club Reprints.) Edinburgh: W. F. Clay.  
J. PRIESTLEY. The Discovery of Oxygen. *Ibid.*

## CHAPTER XI

- J. N. FRIEND. The Chemistry of Combustion. London: Gurney & Jackson.  
H. SCHAPIRO. Chemistry in Industry, Vol. 2, Chap. 13. New York: The Chemical Foundation, Inc.  
A. A. FRIES and C. J. WEST. Chemical Warfare. New York: McGraw-Hill Book Co.

## CHAPTER XII

F. SODDY. Matter and Energy. London: Thornton Butterworth.

## CHAPTER XIII

M. FARADAY. The Chemical History of a Candle. London: Dent & Co.; New York: Harper & Brothers.

W. A. BONE. Coal and its Scientific Uses. London: Longmans, Green & Co.

C. A. MITCHELL. Oil. London: Sir Isaac Pitman & Son.

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## APPENDIX II

### SCALES OF TEMPERATURE—CENTIGRADE AND FAHRENHEIT

ON the Fahrenheit scale of temperature, the melting-point of ice is marked  $32^{\circ}$ , and the boiling-point of water, under normal atmospheric pressure,  $212^{\circ}$ . On the Centigrade scale, these two fixed points are marked  $0^{\circ}$  and  $100^{\circ}$  respectively. Consequently, 180 (or,  $212-32$ ) degrees on the Fahrenheit scale correspond to 100 degrees on the Centigrade scale, or, 9 Fahrenheit degrees are equal to 5 Centigrade degrees. In order, therefore, to convert temperatures on the Fahrenheit scale to temperatures on the Centigrade scale, or *vice versa*, one can make use of the expressions

$$t^{\circ} \text{ C.} = \frac{(t^{\circ} \text{ F} - 32) \times 5}{9} \quad \text{and} \quad t^{\circ} \text{ F} = \frac{t^{\circ} \text{ C} \times 9}{5} + 32$$

On the Absolute scale, the zero of temperature lies at  $-273^{\circ} \text{ C.}$  Consequently,  $t^{\circ} \text{ A.} = t^{\circ} \text{ C.} + 273^{\circ}$ .

## APPENDIX III

### THE METRIC SYSTEM

#### LENGTH.

1 metre is equal to 39.37 inches. The metre is subdivided decimally into 10 decimetres, or 100 centimetres (cm.), or 1000 millimetres (mm.).

1 kilometre (km.)=1000 metres=0.6214 mile.

1 centimetre=0.3937 inch, and 1 decimetre is very nearly equal to 4 inches.

2.54 centimetres=1 inch.

#### VOLUME.

1 litre (lit.)=1000 cubic centimetres (c.c.)=0.0353 cubic feet.  
1 cubic foot=28.32 litre.

1 cubic centimetre=0.0610 cubic inch. 1 cubic inch=16.39 cubic centimetres.

1 litre=1.7598 pints (British)=2.1134 pints (U.S.A.).

1 gallon (British)=4.5460 litres.

1 gallon (U.S.A.)=3.7853 litres.

#### WEIGHT.

The standard of weight is the kilogram. The thousandth part of this is called a gram, and the gram is subdivided into 10 decigrams =100 centigrams=1000 milligrams.

1 cubic centimetre of water at 4° C. weighs 1 gram.

1 gram=15.43 grains.

1 kilogram=2.205 lbs. (Avoir.).

1000 kilograms=2205 lbs.=1 metric ton.

1 oz. avoird.=28.35 grams.

100 grams=3.53 ozs.

# INDEX

- Accumulator, lead, 271
- Accuracy, experimental, 7
- Acetaldehyde, 428
- Acetone, 34, 429
- Acetylene, 218, 421, 429
  - heat of combustion of, 219
- Acheson, Edward G., 189, 280, 411
- Acid, 153
  - acetic, 429
  - benzoic, 454
  - carbolic, 379, 453, 455
  - chamber, 345
  - fatty, 429
  - formic, 429
  - hydrochloric, 277, 359
  - hydrofluoric, 278
  - hypochlorous, 276
  - muriatic, 277
  - nitric, 353, 362, 365, 373, 377
  - nitrous, 365
    - catalytic action of, 326
  - oleic, 434
  - palmitic, 429, 434
  - paratartaric, 446
  - picric, 379, 453, 456
  - pyroligneous, 429, 430
  - silicic, 384
  - stearic, 429, 434
  - sulphuric, 342
    - contact process, 345
    - chamber process, 344
    - properties of, 347
  - sulphurous, 341, 342
  - tartaric, 446
  - tungstic, 325
- Acids, 230, 429
  - definition of, 253, 254
  - detection of, 35
  - strong, 256
  - weak, 256
- Activity, optical, 443
- Adsorption, 331, 405
  - complexes, 407
- Aether, 20
- Affinity, chemical, 318
- Agate, 16, 382
- Age, twilight, of chemistry, 14
- Agent, catalytic, 323
- Ages, dark, 5
  - middle, 5
- Agricola, Georgius, 284
- Agriculture, colloids in, 409
- Air, composition of, 146
  - liquefaction of, 123
  - liquid, 146
  - maintenance of constant composition, 156
  - nitrous, 152
  - weight of, 138
- Alabaster, 348
- Albertus Magnus, 26, 318
- Alchemy, 24
  - Arabian, 24
  - European, 25
  - rise and development of, 21
- Alcohol, 41
  - absolute, 426
  - amyl, 426
  - and water, distillation of, 41
  - butyl, 426
  - ethyl, 424
    - denaturing of, 426
  - iso-amyl, 426
  - iso-butyl, 426
  - iso-propyl, 428
  - methyl, 332
  - origin of term, 423
  - propyl, 426, 428
  - wood, 34
- Alcohols, 423
- Alcool vini, 423
- Aldehydes, 428
- Alizarin, 17, 457
- Al kali (al qali)*, 357
- Alkali waste, 358
- Alkalis, 230
  - definition of, 253, 254
  - detection of, 35
  - strong, 256
  - weak, 256
- Allotropic modifications, 177, 338
- Allotropy, 177
  - of sulphur, 338
- Alloys, 287, 288
  - aluminium, 314
  - copper, 303

- Alloys, production of, by Egyptians, 22  
 Alpha particle, nature of, 83  
 Alum, potash, 314  
 Aluminum, 313  
   — bronze, 314  
   — silicate, 385  
   — soaps, 435  
 Alundum, 280  
 Amalgams, 306  
 Amatol, 380  
 Amethyst, 16, 382  
 Ammonia, 369, 370, 376  
   — combustion of, 373  
   — heat of formation, 371  
   — soda process, 359  
   — synthesis of, 371  
   — use in refrigeration, 372  
 Ammonium, 369  
   — chloride, 270, 369  
   — cyanate, 413, 418  
   — hydroxide, 369  
   — nitrate, 146, 366, 373  
   — phosphate, 374  
   — sulphate, 369, 376  
 Amorphous solids, 126  
 Analysis, 35  
   — positive ray, 90  
 Anaximenes, 19  
 Andrews, Thomas, 121  
 Ångström unit, 129  
 Anhydrides, 365  
 Aulne, 455  
 Anions, 264  
 Anode, 265  
 Anthracene, 456  
 Anthracite, calorific value of, 194  
 Anthraquinone, 457  
 Antimony sulphide, 16  
   — — use in matches, 177  
 Aqua fortis, 363  
   — regia, 290, 363  
 Aquinas, Thomas, 306  
 Archimedes, 6  
 Argol, 427  
 Argon, 158, 160  
   — discovery of, 160  
   — isotopes of, 91  
   — preparation of, 162  
   — properties of, 162  
   — use of, in electric lamps, 163  
 Aristophanes, 5  
 Aristotle, 4, 20  
 Arrhenius, Svante August, 25, 264  
 Arsenious sulphide, colloidal, 406  
 Aspidin, Joseph, 388  
 Assur-bani-pal, 385  
 Aston, F. W., 90  
 Asymmetry, molecular, 449  
 Atmosphere, gases of the, 145  
 Atom, indivisible, postulate of, 55, 87  
 Atom, nucleus of an, 85  
   — structure of, 86  
 Atomic weights based on molecular weights, 135  
   — — determination of, 131  
 Atoms, 21  
 Autocatalysis, 326  
 Avicenna, 25  
 Avogadro, Amedeo, 58, 106  
 Avogadro's number, 114, 115  
 Azote, 146  
 Babbit metals, 307  
 Bacon, Francis, 4, 6, 30, 34  
   — Roger, 6, 26, 354  
 Bakehlte, 428  
 Balard, Antoine Jérôme, 277  
 Balsams, 18, 452  
 Bancroft, Wilder D., 404  
 Barger G., 278  
 Barilla, 357  
 Basic slag, 374  
 Bauer, Georg, 284  
 Bauxite, 314  
 Bayley, T., 72  
 Becher, Johann Joachim, 142, 209  
 Becquerel, Henri, 78  
 Beddoes, Thomas, 260  
 Beer, 17, 427  
   — kaffir, 17  
 Bees-wax, 198  
 Bell metal, 303  
 Bellows used by Egyptians, 138  
 Benjamin, 455  
 Benzene, 204, 454, 455  
   — formula of, 419  
   — homologues, 454  
 Benzoin gum, 455  
   — oleum, 454  
 Benzole, crude, 452  
 Benzoline, 205  
 Berginisation, 208  
 Bergius, F., 208  
 Bergman, Torbern Olof, 49, 50, 369  
 Berkeley, Earl of, 245  
 Bernoulli, Daniel, 104  
 Berthollet, Claude Louis, 56, 276, 366  
 Beryl, 16  
 Berzelius, Jöns Jakob, 61, 131, 323, 382, 412  
 Bessemer, Henry, 295  
   — process, 295  
 Bevan, Edward John, 441  
 Beverages, alcoholic, 426  
 Birkeland, Kristian, 364  
 Biscuit, 386  
 Bisque, 386  
 Black, Joseph, 49, 51, 120, 139, 145, 154  
 Black-lead, 188  
 Blanchard, A. A., 265

- Blast furnace, 293  
 Bleaching powder, 276, 359  
 Blowpipe, oxy-acetylene, 219  
 — oxy-coal-gas, 216  
 — oxy-hydrogen, 223  
 Blue ground, 185  
 — print, 302  
 Bluestone, 304  
 Boerhaave, 52, 318  
 Boiling-point, dependence of, on pressure, 34  
 Bordeaux mixture, 304  
 Bort, 188  
 Bouquet of wines, 427, 432  
 Boyle, Robert, 32, 33, 34, 35, 99, 423  
 Brand, Henning, 175  
 Brandy, 426  
 Brass, 17, 303  
 Brimstone (brennestone), 335, 338  
 Brisance, 378  
 Britannia metal, 307  
 Bromine, 277, 278  
 Bronze, 17, 307  
 Bronzes, 303  
 Brown, Robert, 112  
 — Samuel, 36  
 Brownian movement, 112, 403  
 Buchner, Edward, 329  
 Buffon, 112  
 Bunsen, Robert Wilhelm, 165, 215  
 — burner, 215  
 Butane, 203, 420  
  
 Cabot, 5  
 Cæsium, discovery of, 165  
 Cairngorm, 382  
 Calcite, 389  
 Calcium bicarbonate, 389  
 — bisulphite, 439  
 — carbide, 218, 370  
 — carbonate, 376, 388  
 — chlorohypochlorite, 276  
 — cyanamide, 370  
 — hydroxide, 229  
 — phosphate, 347  
 — sulphate, 376  
 — sulphide, 340  
 Caliche, 356  
 Calomel, 306  
 Calorie, 136, 180  
 Calorific values, 194  
 Calx, 139  
 Cambacères, 199  
 Candles, 197  
 Cannizzaro, Stanislao, 108, 134  
 Carat, 186  
 Carbides, 189  
 Carbohydrates, 437  
 Carboloy, 312  
 Carbon, allotropic forms of, 183  
 Carbon amorphous, heat of combustion of, 189  
 — atom, asymmetric, 451  
 — circulation of, in nature, 193  
 — combustion of, 153  
 — dioxide, 154  
 — — preparation of, 154  
 — — properties of, 155  
 — — solid, 156  
 — — test for, 156  
 — — use for refrigerators, 156  
 — heat of combustion of, 181  
 — monoxide, 182  
 — — combustion of, 183  
 — — poisoning by, 183  
 Carbonado, 188  
 Carborundum, 280  
 Carboxyhæmoglobin, 183  
 Carboxyl group, 429  
 Carlisle, Anthony, 258  
 Carnallite, 352  
 Carnelian, 16, 382  
 Cassia, 18  
 Cassiterite, 307  
 Cassius, purple of, 407  
 Castor oil, 18  
 Catalysis, 317, 322, 323, 372  
 — contact, 327  
 — in heterogeneous systems, 326  
 — in industry, 331  
 — mechanism of, 330  
 — negative, 324, 326  
 — positive, 324  
 Catalyst, 323  
 — definition of, 323  
 Catalysts, poisoning of, 330  
 Catalytic action, 218  
 Cataphoresis, 406  
 Cathode, 265  
 Cations, 264  
 Cause and effect, 9  
 Caustic, lunar, 282  
 Cavendish, Henry, 50, 139, 145, 158, 363  
 Celanese, 441  
 Cell, Daniell, 268  
 — dry, 271  
 — Knowles', 279  
 — Leclanché, 270  
 — Nelson, 274  
 — voltaic, 258, 268  
 Cellon, 442  
 Cellophane, 441  
 Celluloid, 441  
 Cellulose, 194, 377, 439  
 — acetate, 441  
 — calorific value of, 194  
 — glucose from, 439  
 — nitrates, 377, 440  
 Cement, 387  
 — Portland, 388



- Cera, 217  
 Cerussa, 310  
 Chalcedony, 382  
 Chalk, 388  
 Chancel, 174  
 Chaptel, Jean Antoine, 146  
 Charcoal, 15, 190  
   — adsorptive power of, 190  
 de Chardonnet, Count Hilaire, 440  
 Charlemagne, 5  
 Charles, Jacques Alexandre, 101  
 Chaucer, 282  
 Chemistry, aim and scope of, 36  
   — ancient knowledge of, 15  
   — and electricity, 257  
   — Arabic, 24  
   — dawn of, 33  
   — derivation of, 16  
   — fundamental laws of, 49  
   — in space, 449  
   — laws of, and atomic theory, 53  
   — organic, rise of, 412  
   — pneumatic, 49  
   — twilight age of, 14  
 Chevreul, Michel Eugène, 432  
 Chilo saltpetre, 278, 355, 356, 375, 376  
 China salt, 354  
 Chlorine, 275, 277, 359  
   — isotopes of, 91  
   — sterilisation of water by, 225  
 Chloroform, 422  
 Chrome steel, 297  
 Chromium, 297  
 Chrysocolla, 16  
 Chrysoprase, 382  
 Cinnabar, 16, 306  
 Cinnamon, 18  
 Civilisation, prehistorical, 14  
 Clark, Thomas, 227  
 Classification of the sciences, 12  
   — periodic, of the elements, 72  
 Clausius, Rudolf, 104  
 Clay, 385  
   — china, 385  
 Clayton, John, 210  
 Clement-Desormes, 346  
 Cleveite, helium from, 165  
 Coal, 195  
   — calorific value of, 194  
   — distillation of, 196  
   — production of liquid fuel from, 208  
 Coal-gas, 210  
   — calorific value of, 215  
   — composition of, 213  
   — enriching of, 214  
   — introduction of, 210  
   — luminosity of, 214  
   — manufacture of, 211  
 Coalite, 197  
 Coal-tar, 197, 452  
 Cobalt, 305  
 Cohen, Ernst, 307  
 Coke, 197  
 Colburn, Irving W., 394  
 Coleridge, 368  
 Collecting of facts, 6  
 College, Invisible, 34  
   — Philosophical, 34  
 Collodion, 378  
 Colloids, 401  
   — electric charge on, 405  
   — emulsoid, 405, 409  
   — — protective action of, 409  
   — hydrophile, 405  
   — hydrophobe, 405  
   — lyophile, 405  
   — lyophobe, 405  
   — suspensoid, 405  
   — — precipitation of, 406  
 Combination of gases by volume, 105  
 Combustion, as chemical reaction, 172  
   — as oxidation process, 173  
   — explanation of, 141, 145  
   — heat of, 181  
   — phenomenon of, 138  
   — phlogiston theory of, 142  
   — slow, 170  
   — spontaneous, 171  
 Composition of earth's crust, 46  
   — of terrestrial matter, 46  
   — total, of the earth, 47  
 Compound, 37  
 Compounds, 42  
   — aliphatic, 419, 422  
   — aromatic, 419, 452  
   — constant composition of, 43  
   — organic, 413  
 Concrete, 388  
 Condenser, 40  
 Congreves, 176  
 Constitution, 414, 415  
   — atomic, 75  
   — — diagrammatic representation of, 92  
   — electronic, and valency, 91  
 Copper, 16, 302  
   — alloys, 303  
   — carbonate, 16  
   — catalytic action of, 325  
   — electrolytic, 303  
   — nitrate, 304  
   — oxide, 16  
   — refining of, 302  
   — salts, 303  
   — silicate, 16  
   — sulphate, 304, 349  
 Coral, 388  
 Cordite, 379  
 Corundum, 315  
 Cotton, 377  
   — mercerised, 441

Couper, Archibald Scott, 416, 417  
 Couronne de tasses, 258  
 Courtois, Bernard, 277  
 Co-valency, 93  
 Cracking, 206  
 Cream of tartar, 427  
 Cresolin, 456  
 Cresols, 453, 456  
 Cronstedt, A. F., 305  
 Crookes, William, 77, 165, 375  
 — tube, 76  
 Cross, Charles Frederick, 441  
 Cryolite, 314  
 Crystal, 397  
 — hemihedral, 447  
 — holohedral, 447  
 — lattice, 128  
 — — dimensions of, 128  
 Crystallisation, velocity of, 125  
 Crystalloids, 401  
 Crystals, enantiomorphic, 448  
 — growth of, 125  
 — snow, 127  
 — X-ray examination of, 128  
 Curie, Madame, 79, 80  
 — Pierre, 80

Dag, 411

Dalton, John, 54, 56, 57  
 Daniell, John Frederic, 268  
 Davy, Humphry, 7, 170, 214, 258, 259,  
 275, 312, 326, 345, 367  
 Deacon, H. W., 359  
 Deacon's process, 359  
 Deduction, 3, 10  
 Deliquescence, 157  
 Deltas, formation of, 407  
 Democritus, 21  
 Dendrites, 127  
 Density, current, 273  
 — gas, and molecular weight, 108  
 Desiccator, 347  
 Detonating lock, 377  
 Dewar, James, 123  
 Dextrin, 427  
 Dialyser, 384  
 Dialysis, 384, 401  
 Diamond, 180  
 — crystal, model of, 129  
 — Cullinan, 186  
 — heat of combustion of, 184  
 Diamonds, occurrence of, 184, 185, 187  
 Diastase, 425  
 Diatoms, 383  
 Diffusion, 97  
 — and osmotic pressure, 238  
 Diocletian, 23  
 Dips, 198  
 Dissociation, electrolytic, 253  
 Disaccharides, 438

Distillate, 40  
 Distillation, 40  
 — early apparatus, 24  
 Doberner, Johann Wolfgang, 68, 152  
 327  
 Drake, 5  
 Drugs, 18  
 Dry cleaning, 205  
 Dryden, 9  
 Dudley, Dud, 193  
 Duhamel du Monceau, Henri Louis, 357  
 Dulong, Pierre Louis, 136  
 Dumas, Jean Baptiste, 133, 379  
 Dumnite, 380  
 Duralumin, 315  
 Dutch metal, 303  
 Dyang, 17, 407  
 Dyes, ancient, 17  
 Dynamics, chemical, 318  
 Dynamite, 378

Earth, age of, 84  
 Earthenware, 386  
 Edgeworth, Maria, 367  
 Efflorescence, 231  
 Egyptians, chemical knowledge of, 16  
 — medical knowledge of, 18  
 Ekasilicon, 70  
 Electro-chemistry, birth and develop-  
 ment of, 257  
 Electrodes, 222, 250  
 Electrolysis, 250  
 — laws of, 267  
 — mechanism of, 264  
 — of water, 222  
 Electrolytes, 249  
 — strong, 256  
 — weak, 256  
 Electron, 86  
 — mass of, 77  
 Electrons, 77  
 — planetary, 92  
 Electroplating, 273  
 Electroscope, gold-leaf, 79  
 Electrovalency, 93  
 Electrum, 16  
 Element, 35, 37  
 Elements, 42  
 — chemical, 44, 45  
 — classification of, 47  
 — of Aristotle, 20  
 — of Empedocles, 20  
 Elinvar, 297  
 Elixir, 26  
 Emery, 315  
 Empedocles, 20  
 Enamel, 17  
 Enantiomorphic forms, 449  
 Energy, 179  
 — conservation of, 180

- Energy, electrical, 271  
 — kinetic, 179  
 — mechanical, 180  
 — potential, 179  
 — sub-atomic, 94  
 Enquiry, philosophic, age of, 3  
 Enzyme, 329  
 Enzymes as catalysts, 328  
 Epicurus, 21  
 Epsom salts, 349  
 Equations, chemical, 59, 64  
 Equilibrium, 320, 321  
 — influence of temperature on, 322  
 — metastable, 235, 238  
 Equivalence, 132  
 Equivalent, 133  
 — electrochemical, 268  
 Equivalents, 132  
 Erumoid, 428  
 Essence of mirbane, 455  
 Ester, 431  
 Esterification, 432  
 Esters, 430  
 Ethane, 202  
 Ether, diethyl, 430  
 — methylated, 431  
 Ethers, 430  
 Ethyl, 422, 430  
 — alcohol, 424  
 — — denaturing of, 424  
 — — production of, 424  
 — benzene, 453  
 — chloride, 422  
 Ethylene, 203, 421  
 Eupyrion, Hertner's, 174  
 Experiment and observation, 6  
 Explosives, 376  
 — disruptive, 378  
 — propulsive, 378  
 Extract, 427  
 Eyde, Samuel, 364  
  
 Facts, collecting of, 6  
 — difficulties in ascertaining, 7  
 Faience, 17  
 Faraday, Michael, 120, 251, 259, 261, 267, 372, 403, 452, 454  
 Faraday (unit charge), 254, 267  
 Fats, 429  
 — natural, 432  
 Felspars, 385  
 Fermentation, 328  
 Fernbach, Auguste, 429  
 Ferrous oxide, 301  
 — salts, 301  
 — sulphate, 301  
 — sulphide, 341  
 Ferric chloride, 301  
 — oxide, 301  
 — salts, 301  
 Ferric salts, reduction by light, 301  
 — sulphate, 301  
 Fertilisers, nitrogenous, 373, 376  
 Filtration, 39  
 — through soil, 408  
 Fire extinguishers, 155  
 — origin of, 168  
 — production of, 168, 174  
 Fire-air, 143  
 Fire-damp, 98, 170, 202  
 Flame, extinction of, by cooling, 169  
 — luminosity of, 214  
 Flash-point, 206  
 Flint, 382  
 — weapons, early, 14  
 Flotation process, 283  
 Fluorine, 277, 278  
 Foamite, 155  
 Fog-tracks of alpha particles, 81, 87  
 Force, electromotive, 271  
 Formaldehyde, 428  
 Formalin, 428  
 Formula, empirical, 137  
 Formulae, 59, 63  
 — calculation of, 137  
 — constitutional, 418  
 — graphic, 67, 417  
 — structural, 418  
 Forsyth, Alexander John, 377  
 Fourcault, Emile, 394  
 Frankincense, 18  
 Frankland, E., 67  
 Frasch, Herman, 336  
 Freezing-point, 124  
 Fresnel, Augustin Jean, 9, 359  
 Friction lights, 175  
 Fructose, 424, 438  
 Fruit essences, artificial, 432  
 von Fuchs, Johann Nepomuk, 384  
 Fuels, gaseous, 209  
 — liquid, 199  
 — solid, 193  
 Fur, 226  
 Fusel oil, 425, 426  
 Fusion, latent heat of, 121  
  
 Galalith, 428  
 Galena, 16, 309  
 Galileo, 138  
 Galvani, Luigi, 257  
 Gas cooker, 216  
 — equation, general, 110  
 — from coal, 209  
 — laughing, 367  
 — natural, 209  
 — origin of term, 96  
 Gases, kinetic theory of, 103  
 — liquefaction of, 120  
 — of the atmosphere, 138, 145  
 — permanent, 121

- Gases, rare, 158  
 — — spectroscopic identification, 163  
 — — solubility of, 234  
 — — volume of gram-molecular weight, 110  
 — — — pound-molecular weight, 182  
 Gasoline, 205, 206  
 Gay-Lussac, Joseph Louis, 102, 105, 365  
 Geber, 24, 282, 310, 362  
 Geissler tube, 164  
 Gel, 406  
 Gelatine, blasting, 379  
 Germanium, 71  
 German silver, 303  
 Gibbon, 23, 29, 353  
 Gin, 426  
 Glass, 17, 391  
 — coloured, 397  
 — devitrification of, 126, 397  
 — manufacture of, 391, 392, 393  
 — patent plate, 395  
 — silvering of, 398  
 — stained, 397  
 — table-ware, 392  
 — window, 392  
 Glauber, Johann Rudolf, 277, 343, 362, 384  
 Glauber's salt, 349  
 Glucose, 424, 438  
 Glycerol (glycerine), 433, 436  
 Glyceryl butyrate, 434  
 — nitrates, 378  
 Gob fires, 172  
 Gold, 16, 288  
 — chloride, 290  
 — colloidal, 403  
 — currency, 290  
 — extraction of, 288  
 — fineness of, 290  
 — fool's, 293  
 — potable, 403  
 Graham, Thomas, 98, 400  
 Gram-molecule, 110  
 — volume of, 110  
 Graphite, 188  
 — artificial, 189  
 — crystals, arrangement of atoms in, 189  
 — deflocculated, 411  
 — heat of combustion of, 184  
 Greek fire, 353  
 Grotta del cane, 154  
 von Guericke, Otto, 34, 99  
 Guillaume, Charles Edouard, 298  
 Guldberg, Cato Maximilian, 319  
 Gum, British, 427  
 Gun-cotton, 377, 378, 379  
 Gun metal, 303  
 Gunpowder, 353, 354, 377, 378  
 Gypsum, 348, 376  
 Haber, Fritz, 371  
 Hadfield, Robert A., 297, 298  
 Hæmatite, 293  
 Hales, Stephen, 97, 369  
 Hales' apparatus for collecting gases, 97  
 Hall, C. M., 34  
 Halogen derivatives, 422  
 Halogens, 277, 278  
 Hampson, W., 123  
 Hardness of water, permanent, 227  
 — — — temporary, 227  
 Harrington, C. R., 278  
 Harrison, John, 344  
 Harrow, Benjamin, 69  
 Hartley, E. G. J., 245  
 Hartshorn, spirits of, 369, 372  
 Heat, atomic, 136  
 — latent, of fusion, 121  
 — — — vaporisation, 120  
 — mechanical equivalent of, 180  
 — of reaction, 180  
 — specific, 136  
 Helium, 83, 158, 165  
 — discovery of, 165  
 — in natural gas, 165, 209  
 — in radioactive minerals, 165  
 — lifting power of, 166  
 — liquefaction of, 165  
 — properties of, 165  
 — spectrum of, 164  
 van Helmont, Jean Baptiste, 96  
 Hemp, 18  
 Henbane, 18  
 Henry, William, 234  
 Heptane, 205  
 Heraclitus, 20  
 Hermes Trismegistos, 23  
 Hero of Alexandria, 101  
 Herodotus, 391  
 Hérault, Paul L. V., 314  
 Herschel, John F. W., 447  
 Hexane, 205  
 Hippocrates, 318  
 von Hofmann, August Wilhelm, 455  
 Holy fire of Baku, 202  
 Homer, 18  
 Homology, 453  
 — and isomerism, 453  
 Hooke, Robert, 139  
 Hopcalite, 183  
 Howard, Edward Charles, 377  
 von Humboldt, Alexander, 41, 105  
 Humidity, relative, 157  
 Hyatt, 441  
 Hydrocarbon, saturated, 202  
 — unsaturated, 203  
 Hydrocarbons, 198, 420  
 — halogen derivatives of, 422  
 — saturated, 420  
 — unsaturated, 421

- Hydrogen, 220  
 — atom, mass of, 77  
 — bromide, 278  
 — chloride, 277, 358  
 — electrolytic production of, 278  
 — fluoride, 278  
 — from water gas, 332, 333, 376  
 — heat of combustion of, 182  
 — lifting power of, 223  
 — occlusion of, 223  
 — peroxide, 231  
 — preparation of, 220  
 — properties of, 222  
 — sulphide, 340  
 — sulphuretted, 340  
 Hydrogenation of oils, 436  
 Hydrolysis, 424, 432  
 Hydronc, 221  
 Hyoseyamus, 18  
 Hypothesis, 9  
  
 Iatro-chemistry, 30  
 Ibn Sina, 25  
 Ice and salt as freezing mixture, 34  
 — dry, 156  
 — latent heat of fusion, 229  
 Iceland spar, 389  
 Ignis fatuus, 202  
 Ignition point, 168, 169  
 Illuminants, gaseous, 209  
 — liquid, 199  
 — solid, 193, 197  
 Imhotep, 2  
 Indigo, 17  
 Indigotin, 456  
 Induction, 3, 8  
 Industries, electro-chemical, 273  
 Ink, India, 191  
 — marking, 291  
 — writing, 301  
 Institution, Royal, 260, 263  
 Invar, 297  
 Inversion, 438  
 Invertase, 424  
 Iodine, 277, 278  
 Iodoform, 423  
 Ionisation, 264  
 — degree of, 255  
 Ionium, 83  
 Ions, migration of, 265  
 Iron, 16, 292  
 — carbonate, 293  
 — cast, 294  
 — extraction from ore, 293  
 — galvanised, 301, 309  
 — oxides of, 16  
 — pig, 294  
 — pyrites, 293  
 — wrought, 294  
 Isomerism, 414  
 Isomers, 421  
 Iso-propyl benzene, 453  
 Isotopes, 88, 90  
  
 Jabir ibn Hayyan, 24, 282  
 Janssen, 165  
 Japp, F. R., 418  
 Jeyes' fluid, 235, 456  
 Johnson, Dr., 39  
 Jonson, Ben, 27  
  
 Kamite, 352  
 Kaolin, 15, 385  
 Kaolinite, 385  
 Keats, 167  
 Kekulé, Friedrich August, 416, 418, 452  
 Kelvin, Lord, 85  
 Kermes, 17  
 Kerosene, 205  
 Ketones, 428  
 Kieselguhr, 378  
 Kipp's apparatus, 221  
 Kirchhoff, Gustav Robert, 165  
 Knocking, 207  
 Knowledge, ancient chemical, 15  
 Kobold, 305  
 Krypton, 158, 166  
 — isotopes of, 91  
 Kühne, W., 329  
 Kupfernickel, 305  
  
 Lacquers, 442  
 Lactose, 438  
 Lampblack, 190  
 Lamps used by cave men, 15  
 Landolt, H., 53  
 Lapis lazuli, 16  
 de Laplace, Pierre Simon, 366  
 Lavoisier, Antoine Laurent, 50, 52, 143, 144, 145, 382  
 Law, Boyle's, 99  
 — Dulong and Petit's, 136  
 — Gay-Lussac's, 101, 105  
 — Henry's, 234  
 — of combination of gases, 105  
 — of conservation of mass, 52  
 — of constant composition, 56  
 — — proportions, 91  
 — of diffusion of gases, 98  
 — of mass action, 318  
 — of multiple proportions, 56, 365  
 — of nature, 8  
 — periodic, 68, 69, 88  
 — Prout's, 75  
 — scientific, 8, 9  
 Lawes, John Bennet, 347  
 Lead, 16, 309  
 — action of water on, 309  
 — atomic weight of, 90  
 — carbonate (basic), 310

- Lead dioxide, 310  
 — oxides, 310  
 — red, 310  
 — sulphide, 16, 309  
 — white, 310  
 Lear, Edward, 117  
 Leather, 17  
 — imitation, 442  
 Le Bel, Joseph Achille, 449  
 Leblanc, Nicolas, 358  
 Le Châtelier, Henri Louis, 322  
 — — theorem of, 322, 371  
 Leclanché, Georges, 270  
 Lemery, Nicolas, 412  
 Leucippus, 21  
 von Liebig, Justus, 143, 373, 414, 454  
 Light, polarisation of, 443  
 Light-box, instantaneous, 174  
 Lignite, calorific value of, 194  
 Lime light, 223  
 — slaking of, 230  
 — water, 153  
 Limestone, 388  
 — caves, 389  
 — terraces, 390  
 Limonite, 293  
 von Linde, C., 123  
 Liquefaction of gases, 120  
 Liquid, supercooled, 125  
 Liquids, solubility of, 235  
 Liquor silicium, 384  
 Liquors, alcoholic, 17  
 Litmus, 35, 153  
 Litharge, 310  
 Lithopone, 309  
 Lockyer, Norman, 165  
 Lomonossov, Michael Vassilievitch, 143  
 Lowe, H. A., 441  
 Lubbers, J. H., 393  
 Lucifers, 175  
 Lucretius, 14, 21  
 Lully, Raymond, 29  
 Luminosity of coal-gas, 214  
 Lunar caustic, 291  
 Lustron, 441  
 Lyddite, 380  
 Lysol, 235, 456  
  
 Magic and mysticism, age of, 2  
 Magisterium, 26  
 Magnalium, 315  
 Magnesium, 316  
 — nitride, 145  
 — sulphate, 349  
 Magnetite, 293  
 Magnitudes, molecular, 114  
 Malachite, 16  
 Maltase, 424  
 Maltose, 424, 438  
  
 Malt-sugar, 424  
 Mandragora, 18  
 Mandrake, 18  
 Manganese, oxide of, 16, 152, 270, 275  
 Manley, J. J., 53  
 Mantle, incandescent, 217  
 Marble, 388  
 Marcus Græcæus, 354  
 de Marignac, Jean Charles, 133  
 Marsh gas, 202  
 van Marum, 191  
 Mashing, 425  
 Maspero, G., 3  
 Mass action, law of, 318  
 Match, safety, 177  
 — strike anywhere, 178  
 — Swedish, 177  
 Matches, 176  
 Materials, heterogeneous, 38, 39  
 — homogeneous, 38, 39  
 — known to the ancients, 16  
 Matter and energy, 179  
 — classification of, 43  
 — continuity of, 20  
 — terrestrial, composition of, 46  
 Maxwell, James Clark, 104  
 Mayow, John, 96, 139, 143  
 Mead, 17  
 Medicine, Egyptian, 3, 18  
 Mélinite, 380  
 Melting-point, 124  
 Membrane, semi-permeable, 240  
 Mendeléeff, Dmitri Ivanowitsch, 69, 70, 71, 74  
 Mercer, John, 441  
 Mercuric chloride, 306  
 — salts, 306  
 — sulphide, 16, 306  
 Mercurous chloride, 306  
 — salts, 306  
 Mercury, 16, 306  
 — calx of, 144  
 — fulminate, 377  
 — oxide, 144  
 — — decomposition of, 42  
 — sulphide, 16, 306  
 "Mercury," 25  
 — and "Sulphur" theory, 25  
 — "sulphur" and "salt" theory, 31  
 Mesothorium I., 83  
 Metal, definition of, 282  
 — white, 303  
 Metallography, 286  
 Metallurgy, 283  
 Metals, 47, 281, 288  
 — alkali, 312, 313, 350  
 — Arabic views regarding, 25  
 — base, 282  
 — crystalline structure of, 286  
 — fusible, 310

- Metals in antiquity, 281  
 — noble, 282  
 — non-ferrous, 302, 312  
 — structure of, 286  
 Methane, 201  
 Methanol, 332, 423  
 Method, modern scientific, 6  
 Methyl, 422  
 — alcohol, 423  
 — chloride, 422  
 Metric system, 465  
 Meyer, Lothar, 69, 135  
 Micro-balance, 8  
 Microcosmic salt, 175  
 Millikan, R. A., 114  
 Minimum, 310  
 Mirrors, glass, 398  
 Mitchell, Samuel Latham, 367  
 Mixture, 37, 39  
 — homogeneous, 42  
 Mixtures, homogeneous, and compounds, 43  
 Modifications, allotropic, 177  
 Moissan, Henri, 277  
 Moisture, catalytic action of, 324  
 Molecular magnitudes, 114  
 — structure, theory of, 415  
 — weight and atomic weight, 135  
 — — and osmotic pressure, 245  
 — — of dissolved substances, 245, 246  
 Molecule, 58, 106  
 Molecules, objective reality of, 111  
 Molinari, E., 336  
 Molybdenum, 301  
 Molybdic acid, catalytic action of, 325  
 Monazite, 217  
 Mond, Ludwig, 305  
 — process, 305  
 Monel metal, 303  
 Monosaccharides, 438  
 Mordant, 408  
 Mordants, 17  
 Morley, Edward W., 229  
 Morse, H. N., 244  
 Mortar, 387  
 Movement, Brownian, 112  
 Mucor Boulard, 425  
 Muntz metal, 303  
 Murdoch, William, 210  
 Must, 427  
 Mustard gas, 203  
 Myrrh, 18  
 Mysticism and magic, age of, 2  
  
 Naphtha, burning, 453  
 — solvent, 453  
 Naphthalene, 456  
 Naphthalenes, 204  
 Natron, 357  
 Nature, simplicity of, 8  
 Nature, uniformity of, 8  
 Nelson, H. R., 274  
 Neon, 158, 166  
 Newlands, J. A. R., 69  
 Newton, 52, 54  
 Nicholson, William, 258  
 Nichrome, 305  
 Nickel, 304  
 — carbonyl, 305  
 — catalytic action of, 437  
 — — surface of, 33  
 — plating, 305  
 Niton, 166  
 Nitre plantations, 355  
 Nitric oxide, 364, 373  
 Nitro-benzene, 455  
 Nitro-cellulose, 440  
 Nitro-cottons, 378  
 Nitrogen, 145, 362  
 — assimilation by plants, 374  
 — atmospheric, fixation of, 364, 375  
 — fixation of, 369  
 — from liquid air, 146  
 — oxides of, 365  
 — peroxide, 363, 365, 369  
 — tetroxide, 363  
 Nitrogene, 146  
 Nitro-glycerine, 378, 379, 436  
 Nitrous oxide, 366  
 Nobel, Alfred Bernhard, 378  
 Nollet, Jean Antoine, 240  
 Non-electrolytes, 249  
 Non-metal, definition of, 283  
 Non-metals, 47  
 Northmore, Thomas, 120  
 Noyes, A. A., 11, 265  
 Number, atomic, 87, 88  
 — — and periodic law, 88  
 — Avogadro's, 114, 115  
 — of molecules in a cubic centimetre of gas, 84  
  
 Observation and experiment, 4  
 Ochres, 293  
 Octane, 205  
 Octaves, law of, 69  
 Octet, 92  
 Oil, burning, 205  
 — gas, 205  
 — light, 452  
 — paraffin, 205  
 — shale, 198, 208  
 — solar, 205  
 Oils, anthracene, 452  
 — carbolic, 452, 453  
 — creosote, 452  
 — fragrant, 452  
 — fuel, 205, 206  
 — hydrogenation of, 436  
 — lubricating, 205

- Oils, middle, 453  
   — natural, 432  
 Olefines, 203  
 Oleum, 345  
   — silicium, 384  
 Onnes, Kammerlingh, 165  
 Onyx, 382  
 Opal, 383  
 Open-hearth process, 295  
 Opium, 18  
 Osmosis, 240  
 Osmotic pressure, 238, 240  
   — — and molecular weight, 245  
   — — measurement of, 241  
 Ostwald, Wilhelm, 323, 373  
 Oxidation, 153  
 Oxides, 153  
 Oxy-acetylene flame, 219  
 Oxygen, 144, 147, 148, 150, 151, 369  
   — electrolytic production of, 278  
   — from liquid air, 146  
   — preparation of, 152  
   — properties of, 152, 153  
 Oxy-hydrogen blowpipe, 223  
 Ozone, 191  
  
 Paper, 439  
 Paracelsus, 27, 30, 309, 423  
 Paraffin, solid, 205  
   — wax, 198  
 Paraffins, 203  
 Particles, colloid, dimensions of, 404  
   — — electric charge on, 405  
   — — scattering of light by, 404  
 Paste, 397  
 Pasteur, Louis, 328, 445, 446, 447, 448, 449  
 Pearls, 389  
 Pears, essence of, 432  
 Peat, calorific value of, 194  
 Pelican, 29  
 Pentane, 205  
 Peptase, 427  
 Peptisation, 411  
 Percussion cap, 378  
 Permutit, 227  
 Perrin, Jean, 87, 113  
 Pertite, 380  
 Petit, Alexis Thérèse, 136  
 Petrol, 205  
 Petroleum, 199  
   — benzine, 205  
   — composition of, 201  
   — crude, 204  
   — ether, 205  
   — fractional distillation of, 204  
   — occurrence of, 199  
   — origin of, 201  
 Petronius, 395  
 Pewter, 307  
  
 Pfeffer, Wilhelm, 241  
 Phenol, 379, 455  
   — solubility of, 235  
 Phenols, 455  
 Phillips, Peregrine, 345  
 Philosopher's stone, 26, 27, 28, 29  
 Philosophic enquiry, age of, 3  
 Philosophy, Greek, 3, 19  
 Phlogiston, 142  
   — theory, 141  
   — — overthrow of, 143  
 Phosphor-bronze, 303  
 Phosphorus, 145, 175  
   — allotropic forms of, 177  
   — combustion of, 153  
   — in plants, 374  
   — mirabilis, 175  
   — red, 177  
   — smoke screen, 176  
   — sulphide, use in matches, 177  
   — white, 175  
   — — use in matches, 176  
 Phossey jaw, 176  
 Pigments used by cave men, 15  
 Pine-apple, essence of, 432  
 Pitch, 452  
 Pitchblende, 80  
 Plaster of Paris, 348, 387  
 Platinite, 292, 298  
 Platinum, 291  
   — catalytic action of, 327, 345, 373  
 Plato, 3, 4  
 Pliny, 22, 184, 289, 310, 335, 342, 391, 434  
 Plücker, Julius, 76  
   — tube, 164  
 Plumbago, 188  
 Poison valley of Java, 154  
 Porcelain, 386  
 Potash, 350  
 Potassium, 313  
   — bromide, 278  
   — chlorate, 151, 276  
   — chloride, 374  
   — — solubility of, 355  
   — hydrogen tartrate, 427  
   — hydroxide, 275  
   — in plants, 374  
   — nitrate, 353, 355  
   — — solubility of, 355  
   — salts, 350  
   — — effect of, on growth of plants, 351  
   — sulphate, 374  
 Pozzuolana, 387  
 Prehistory, 14  
 Pressure, normal, 103  
   — vapour, 118  
 Priestley, Joseph, 139, 142, 144, 149, 310, 341, 366, 369  
 Prima materia, 19



- Promoter, 325  
 Propane, 202, 420  
 Properties, specific, 38  
 Propyl benzene, 453  
 Propylene, 203  
 Proton, 85  
 Proust, Joseph Louis, 56  
 Proportions, multiple, law of, 56  
 Prout, William, 75  
 Prout's law, 75  
 Pulp, sulphite, 439  
 Purple of the ancients, 17  
 — Tyrian, 17  
 Pyrex glass, 396  
 Pyrolusite, 15  
 Pythagoras, 19  
  
 Quartz, 382  
 — glass, 383  
 — rose, 382  
 — smoky, 382  
 Quicksilver, 306  
  
 Racemic form, 451  
 Radical, 369, 422  
 Radicals, 422  
 Radioactivity, 75, 78  
 — decay of, 82  
 — disintegration theory of, 83  
 Radium, 80, 82  
 — disintegration of, 82, 89  
 Radon, 82, 166  
 Ramie fibre, 217  
 Ramsay, William, 83, 160, 161, 162, 165, 166  
 Raoult, François Marie, 245  
 Rayleigh, Lord, 160, 162  
 Rayon, 440  
 Rays, alpha, 80  
 — beta, 80  
 — cathode, 76  
 — gamma, 80  
 Reactants, 322  
 Reaction, balanced, 432  
 — heat of, 180  
 — reversible, 320, 321, 432  
 — velocity of, 317, 319  
 Reactions, endothermal, 181  
 — exothermal, 181  
 Reality of molecules, 111  
 Recrystallisation, purification by, 238  
 Receiver, 40  
 Reducing agent, 223  
 Reduction, 183, 223  
 Refraction, double, 389  
 Refrigeration, 372  
 Renaissance, 5  
 Resins, fragrant, 18  
 Resultants, 322  
  
 Rexine, 442  
 Rey, Jean, 56, 139  
 Rhizopus Delemar, 425  
 Robert of Chester, 25  
 Rock crystal, 381  
 Roebuck, John, 344  
 von Röntgen, Wilhelm Konrad, 78  
 Rubber, perishing of, 326  
 Rubidium, discovery of, 165  
 Rubies, artificial, 315  
 Rum, 426  
 Rumford, Count, 260  
 Rupert's drops, 395  
 Rutherford, Daniel, 145, 362  
 — Ernest, 83, 84, 85, 95  
 Rushlight, 198  
  
 Sabatier, Paul, 437  
 Safety lamp, 170  
 Safflower, 17  
 Sal ammoniac, 369  
 Salisbury, Lord, 74  
 Salt, common, 360  
 — — arrangement of atoms in crystal, 130  
 — glaze, 386  
 — hydrates, 230  
 — spirit of, 277  
 Salts, 230  
 — definition of, 253, 254  
 Salt-cake, 358  
 Saltpetre, 353  
 Saltwort, 357  
 Saponification, 432  
 Sapphires, artificial, 315  
 Saratoga Springs, 154  
 Sauria, Charles, 176  
 de Saussure, Nicolas Théodore, 157  
 Scale, 226  
 Scheele, Carl Wilhelm, 139, 143, 147, 148, 275  
 Schimosite, 380  
 Schönbein, Christian Friedrich, 191, 377  
 Science, aim and method of, 1  
 Sciences, biological, 13  
 — classification of the, 12  
 — physical, 13  
 Scott, Walter, 299  
 Searles Lake, 353  
 Season cracking, 303  
 Sea-water, distillation of, 41  
 Sedimentation in rivers, 407  
 Semi-coke, 197  
 Senderens, Jean Baptiste, 437  
 Septon, oxide of, 367  
 Series, homologous, 420  
 Shakespeare, 117  
 Shale, liquid fuel from, 208  
 Sharing of electrons, 93  
 Shaw, J., 378

- Wash, 425  
Washington, H. S., 47  
Water, 223  
— and alcohol, distillation of, 41  
— chemical properties, 229  
— composition, 229  
— expansion, 228  
— glass, 384  
— hard, 226  
— inflammable, 41  
— latent heat of vaporisation, 228  
— mineral, 224  
— of hydration, 230  
— physical properties, 228  
— potable, 225  
— rain, 224  
— river, 224  
— sea, 225  
— softening of, 227  
— specific heat of, 228  
— sterilisation by chlorine, 225  
— vapour in the air, 157  
Water-gas, 215, 221  
— carburetted, 215  
Wax, China, 199  
Wedgwood, Josiah, 386  
Weight, atomic, 58  
— gram-molecular, 110  
— molecular, 64  
— — and gas density, 108  
Weights, atomic, 91  
— — based on molecular weights, 135  
— — determination of, 131  
— molecular and atomic, 135  
von Welsbach, Auer, 217  
Wheat, 374  
Whisky, 426  
Widia, 312  
Will-o'-the-Wisp, 202  
Wilson, C. T. R., 81  
Wine, 17, 427  
Winkler, Clemens Alexander, 71  
Winzer (Winsor), 210  
Wohler, Friedrich, 314, 412, 414  
Wolfram, 312  
Wood, 193  
— calorific value of, 194  
— naphtha, 424  
— petrified, 390  
— spirit, 332, 423  
Wort, 425  
Woulfe, Peter, 379  
  
Xenon, 158, 166  
X-rays, 78  
X-ray tube, 78  
Xylene, meta, 454  
— ortho, 454  
— para, 454  
  
Yeast, 424  
  
Zinc, 309  
— blende, 309  
— crystalline structure of, 286  
— oxide, 309  
— sulphide, 309  
— white, 309  
Zosimos, 23  
Zsigmondy, Richard, 403  
Zymase, 329, 424

THE END

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